

Review

The Protagonism of Biocatalysis in Green Chemistry and Its Environmental Benefits

Viridiana Santana Ferreira-Leitão ^{1,2,*}, Magali Christe Cammarota ³,
Erika Cristina Gonçalves Aguiaras ¹, Lívian Ribeiro Vasconcelos de Sá ^{1,2},
Roberto Fernandez-Lafuente ^{4,*} and Denise Maria Guimarães Freire ^{1,*}

¹ Department of Biochemistry, Federal University of Rio de Janeiro, Avenida Athos da Silveira Ramos, 149, Bloco A, Sala 549-1, Cidade Universitária, CEP 21941-909 Rio de Janeiro, Brazil; erikaaguieiras@gmail.com (E.C.G.A.); livian_sa@yahoo.com.br (L.R.V.d.S.)

² Laboratory of Biocatalysis, Ministry of Science and Technology, National Institute of Technology, Avenida Venezuela, 82, Sala 302, CEP 20081-312 Rio de Janeiro, Brazil

³ Department of Biochemical Engineering, Federal University of Rio de Janeiro, CEP 21941-909 Rio de Janeiro, Brazil; christe@eq.ufrj.br

⁴ Departamento de Biocatálisis, Instituto de Catálisis-CSIC, Campus UAM-CSIC, C/Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

* Correspondence: viridiana.leitao@int.gov.br (V.S.F.-L.); rfl@icp.csic.es (R.F.-L.); freire@iq.ufrj.br (D.M.G.F.); Tel.: +55-21-21231108 (V.S.F.-L.); +34-91-5854941 (R.F.-L.); +55-21-39387360 (D.M.G.F.)

Academic Editor: David D. Boehr

Received: 11 November 2016; Accepted: 22 December 2016; Published: 1 January 2017

Abstract: The establishment of a bioeconomy era requires not only a change of production pattern, but also a deep modernization of the production processes through the implementation of novel methodologies in current industrial units, where waste materials and byproducts can be utilized as starting materials in the production of commodities such as biofuels and other high added value chemicals. The utilization of renewable raw resources and residues from the agro-industries, and their exploitation through various uses and applications through technologies, particularly solid-state fermentation (SSF), are the main focus of this review. The advocacy for biocatalysis in green chemistry and the environmental benefits of bioproduction are very clear, although this kind of industrial process is still an exception and not the rule. Potential and industrial products, such as biocatalysts, animal feed, fermentation medium, biofuels (biodiesel, lignocelulose ethanol, CH₄, and H₂), pharmaceuticals and chemicals are dealt with in this paper. The focus is the utilization of renewable resources and the important role of enzymatic process to support a sustainable green chemical industry.

Keywords: biocatalysts; green chemistry; fuels; energy; chemicals

1. Introduction

Greener processes are no longer just an environmental option, but a strategic choice in the modern economy [1]. The implementation of new production processes founded on the 12 principles of green chemistry [2] requires not only a change in terms of culture and procedures, but, above all, investment, because current chemical processes, which are not optimized and environmental friendly, must be redesigned [3]. Green Chemistry has huge potential and can be applied in different sectors of the Chemical Industry to offer a series of important advantages, such as safer processes and products, reduction in the use of toxic substances and solvents, minimization of waste disposal and emissions, and energy and water savings. Therefore, the design of greener processes should be considered as an investment, optimized processes become cheaper than the traditional ones. In addition, these procedures will help to ensure that production can be carried out in accordance with possible future legal regulations [1,3]. According to Rangarajan, three relevant aspects should be considered in terms

of ecological advantages and cost reductions: (1) The simplification of the total process, by minimizing reaction steps, and the necessity for contaminant solvents and reagents as well as the associated dangers and energy employed for drying and heating at each step; (2) safer production methodologies, utilizing water as solvent, instead of organic ones; and (3) constant production processes with online control and monitoring, together with chemical recycling during the process [4].

Green chemical principles proposed by Anastas and Warner [5] are shown below. This review will mainly discuss biocatalytic or microbial processes for utilization of renewable or residual materials. The following principles will be entirely covered from 1 to 12. In other words, biocatalysis and industrial biotechnology are very important in the progress of the bioeconomy and green chemistry era, as illustrated in Figure 1 (see Sjöström [6] for a discussion of a similar model).

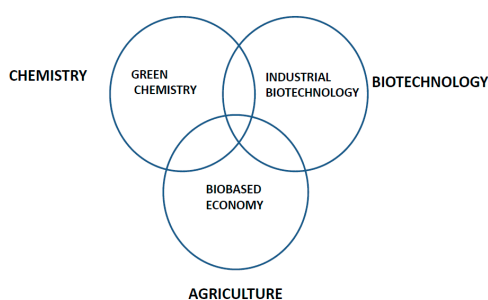


Figure 1. Intersections of fields involved in green processes (adapted from Map of knowledge by Jesper Sjöström—Greenchem Project) [6]. Copyright year 2006 Publisher: Royal Society of Chemistry.

Green Chemistry Principles:

1. Waste prevention instead of remediation
2. Atom economy or efficiency
3. Use of less hazardous and toxic chemicals
4. Safer products by design
5. Innocuous solvents and auxiliaries
6. Energy efficiency by design
7. Preferred use of renewable raw materials
8. Shorter syntheses (avoid derivatization)
9. Catalytic rather than stoichiometric reagents
10. Design products to undergo degradation in the environment
11. Analytical methodologies for pollution prevention
12. Inherently safer processes

In recent years, production and utilization of metabolites from microbial and plant origin have received increasing attention from different industrial sectors, such as fuel, pharmaceutical, food, and chemical. This is due to their potential to replace conventional products that are mainly produced from raw materials of petrochemical origin. Therefore, development of biotechnological processes for obtaining these bioproducts is very important to facilitate and expand their use in diverse industrial segments. The deployment of technologies that enable the reuse of wastes and industrial by-products reduces process costs and adds value to waste materials [7,8]. Agro-industrial and forestry residues, obtained from relevant industrial and economical activities, are useful raw resources for manufacture of renewable stuffs, such as energy, fuels and chemicals. The exploitation of wastes from diverse sources is strategic, as their accessibility is not affected by the controversial competition between food and fuel. Moreover, utilization of waste prevents their accumulation, which helps protect the environment [9].

Agro-industrial activities result in large amounts of liquid and solid wastes that can be used as raw materials to obtain different products of industrial interest. These can be obtained by solid

state or submerged cultivations, or even by enzyme conversion, which constitutes a very relevant process of White Biotechnology or Industrial Biotechnology, as presented in Figure 1. Among the most common residues available are cane molasses, bagasse, cakes and sharps from oilseeds, corn steep liquor, and beer waste. Besides these, agricultural crop residues also include straw, stem, stalk, leaves, bark, seeds/pits, and others obtained from cereals (sorghum, rice, corn, wheat, and barley), as well as a wide variety of industrial effluents [10]. In countries like Brazil and the United States, due to the rapid growth of the biofuel industrial sector (ethanol and biodiesel), fibrous waste and cakes from oilseed have become increasingly abundant [11]. Often, these residues are not fully utilized, even though most of them show great prospective for several biotechnological applications, mainly because of their low cost, accessibility, and chemical and nutritional composition. Therefore, the utilization of these agricultural residues as cheap media for products of biotechnological interest, as well as their indisputable economic advantage, allows the implementation of a sustainable and environmental cycle [12]. The use of agricultural residues to obtain products of biotechnological interest can be divided into different categories, including the following that will be explored in this review: low cost production of biocatalysts; detoxification and nutritional enrichment for the formulation of animal feed, for obtaining generic cultivation media; and other chemical conversions for energy and chemical production.

Similar to a petroleum refinery, future sustainable bioprocesses will have an integrated installation to process a wide variety of raw materials for bioenergy, chemicals, and other valuable products, to maximize the utilization of biomass and diminish waste. The interface among green chemistry, industrial biotechnology, and biobased economy will support a range of important industrial units. The advocacy of biocatalysis and the corresponding environmental benefits are based on the fact that the enzymes and microorganisms are capable of catalyzing the hydrolysis and degrading almost all macromolecules present in agro-industrial materials, with good conversion levels and high degree of specificity. Within this context, the present review contains several examples of the use of residues to obtain value-added products.

2. Biocatalysis in Residues

2.1. Use of Solid Waste to Obtain Biocatalysts

Due to the central role of enzymes in bioprocesses and even in many current industrial processes, several researches have been performed to achieve high-yield, low-cost biocatalysts. Liquid residues, such as crude glycerin, manipuera (residue from the processing of cassava), and molasses, can be used in submerged fermentation (SF). Solid residues (such as husk, oil cakes, bagasse, bran, and fruit seeds) have been employed as cheaper culture media for solid state fermentation (SSF) to yield several biocatalysts [13].

This process has received attention as a promising alternative for industrial enzyme production [14–19], and other products, such as aromas [20–22], pigments [23], biopesticides [24–26], organic acids [27,28], and other biochemicals.

The production of enzymes by SSF has several advantages when compared to the traditional SF, including enhance productivity of the fermentations, higher final products concentration, decrease of catabolic repression, growth of micro-organisms adapted for the use of water-insoluble substrates or mixed growth of several fungi, and decreased request on medium sterility thanks to the low water activity employed in SSF [29]. The high productivity obtained by SSF is because the similarity between cultivation conditions and those of the natural media of filamentous fungi as well as the low protease activity compared to the SF process [29–31]. These advantages have raised the interest of researchers to obtain several biocatalysts of industrial interest, such as lipases [14,32–38], proteases [39–41], cellulases [42,43], xylanases [44,45], pectinases [16,46], amylases [47–49], phytases [50–52], inulinases [53,54], tannases [55,56], and others [57] (Table 1). The metabolic expression of fungi differs according to the type of the residues used as substrate, which

allows the production of enzymes with different features that can be utilized in the biotechnological industry in different forms [58]. Moreover, some biomass characteristics, such as inorganic matter, carbohydrates, protein and lipid content, bulk density, elemental analysis (C, N, H, S), calorific value, particle size distribution, and porosity, alter the performance of the process where they are employed, and should be evaluated according to the purpose of the study [59]. It was demonstrated for example that C/N ratios higher than 10 are advantageous for enzyme production, (e.g., protease, amylase, cellulose, and xylanase) in SSF processes [60].

Table 1. Production of industrial biocatalysts by Solid-State Fermentation.

Solid Substrate	Microorganism	Enzyme	Reference
Babassu cake	<i>Penicillium simplicissimum</i>		[34]
	<i>Penicillium restrictum</i>		[14]
Castor bean waste	<i>Penicillium simplicissimum</i>		[35]
Soybean bran	<i>Penicillium verrucosum</i>	Lipase	[36]
Barley bran	<i>Rhizopus oryzae</i>		[37]
Sugarcane bagasse	<i>Rhizopus homothallicus</i> (IRD13a)		[32]
Wheat bran	<i>Aspergillus niger</i>		[38]
Feather meal supplemented with corn steep liquor	<i>Streptomyces</i> sp. 594		[40]
Soy cake	<i>Bacillus subtilis</i>	Protease	[39]
Wheat bran	<i>Aspergillus oryzae</i> MTCC 5341		[41]
Corn cob residue	<i>Trichoderma reesei</i> ZU-02		[42]
Steam exploded wheat straw	<i>Neurospora sitophila</i>	Cellulase	[43]
Wheat bran, beet pulp, and apple pomace	<i>Chaetomium globosum</i> and <i>Aspergillus niger</i>		[44]
Rice straw	<i>Aspergillus niger</i> KK2 mutant	Xylanase	[45]
Wheat bran	<i>Aspergillus niger</i>		[16]
Dried deseeded sunflower head	<i>Aspergillus niger</i>	Pectinase	[46]
Coconut oil cake	<i>Aspergillus oryzae</i>		[47]
Babassu cake	<i>Aspergillus awamori</i> IOC-3914	Amylase	[48]
Sugarcane bagasse	<i>Aspergillus niger</i>		[49]
Wheat bran, wheat straw, cotton oil cake, and gram bran	<i>Aspergillus oryzae</i> SBS50		[51]
Citrus peel	<i>Aspergillus niger</i>	Phytase	[50]
Mustard cake	<i>Aspergillus flavus</i>		[52]
Rosewood saw dust	<i>Aspergillus heteromorphus</i> MTCC 8818		[55]
Citrus residue	<i>Paecilomyces variotii</i>	Tannase	[56]
Wheat bran	<i>Staphylococcus</i> sp. and <i>Kluyveromyces marxianus</i>		[53]
Sugarcane bagasse and soybean bran	<i>Kluyveromyces marxianus</i>	Inulinase	[54]
Mixture of soybean meal and wheat bran			
Mixture of soybean meal and cottonseed meal	<i>Aspergillus niger</i>	Invertase	[57]

SSF process has the possibility of using agro-industrial residues that are cheap and readily available in several countries including Brazil, India, and the United States [13,34]. Castilho et al. [17] performed an economic balance of the production of the lipase from *Penicillium restrictum* based on SF and SSF. The process using SF was 78% more expensive (total capital investment) than the one utilizing SSF employing babassu cake as substrate, and resulted in lower catabolic repression. This feature of SSF to overcome catabolic repression due to the difficulty of transferring mass of gases and nutrients has been utilized for the production of several microbial enzymes [15,61]. Therefore, the utilization of solid wastes to produce industrial enzymes not only contributes to cost reduction but also adds value to these wastes.

It is relevant to remark that this process presents some drawbacks, such as heat transfer, limitations in on-line monitoring, controlling process parameters and biomass estimation, scale up, and purification of end products [62,63]. However, several researchers have focused on finding the solutions for these challenges.

2.2. Detoxification and Improvement of the Nutritional Quality of Residues for Animal Feed

Another potential application of the agro-industrial residues is in formulation of animal feed. In this case, the SSF process can be used for detoxification and proteic enrichment of the residues to substitute high cost components, such as fish flour and soy bean.

Vegetable sources such as cottonseed meals and cakes are alternatives to traditional protein meals, because of their widespread availability, relatively favorable amino acid composition, low price, and sustainable nature, [64]. However, agro-industrial solid wastes often present anti-nutritional and anti-physiological compounds (such as phytates, tannins, and protease inhibitors) or toxic factors (such as ricin found in castor beans and phorbol esters from *Jatropha curcas*). Such components make these residues unsuitable as supplements in animal feed [35,65]. Although physical and chemical treatments may be used to remove/inactivate these components, these methods are often highly energy-consuming, yielding it economically impracticable when bearing in mind large-scale industrial application.

As an alternative, several researchers have focused on the biological detoxification by SSF as an efficient and cheap method to eliminate these undesirable compounds [35,65–71]. Furthermore, if the waste is not useful after the treatment of detoxification, it may be thrown away in nature without producing soil or water contamination. Brand et al. [65] achieved, through SSF of coffee husk, a 65% tannin and 92% caffeine decontamination employing the fungus *Aspergillus* sp. Hassaan et al. [64] studied the process of SSF to reduce anti-nutritional factors in soybean meal. This product was fermented with *Saccharomyces cerevisiae*, and the fermented meal was used in formulated diets for Nile tilapia *Oreochromis niloticus*. The authors observed that 37.4% of fish meal could be replaced by fermented soybean meal. According to Dey et al. [72] several enzymes, such as proteases, amylases, and lipases are synthesized by microorganisms during SSF. Proteins, polysaccharides and lipids are hydrolyzed by these enzymes producing save products with pleasing aroma, flavor, and textural features. Residue of castor bean was detoxified by Madeira et al. [68] using a strain of *Paecilomyces variotii*. The authors also obtained high production of phytase and tannase. SSF process was also described for the full degradation of phorbol esters catalyzed by *Pseudomonas aeruginosa* of *Jatropha curcas* seed cake [69]. SSF was used to grow *P. simplicissimum* strain in castor bean waste. This fermentation process removed the ricin and decreased the allergenic features of the castor bean waste. Moreover, the production of an acid and heat stable lipase also occurred [35,66,67]. This fermentation process is described in the patent PI0703290-0 [73]. Phengnuam and Suntornsuk [70] reduced the phorbol ester and phytate contents using bacterial fermentation of *J. curcas* seed cake. Veerabhadrapa et al. [71] studied the biological detoxification of *J. curcas* seed cake by *Aspergillus versicolor*, and the contents of phorbol esters, trypsin inhibitors, tannins, and phytates were reduced by 81%, 95%, 38%, and 72%, respectively. Similar results were attained by Zhang et al. [74] using *Morganella morganii* species to biodegrade phorbol esters and curcin by solid-state fermentation.

In addition to the efficient removal of toxic and/or anti-nutritional compounds, SSF can be employed to enhance the nutritional value of the fermented solids through protein enrichment of the residues. This enrichment is possible through the growth of microorganisms “generally recognized as safe” or “GRAS” such as *A. niger*, *A. oryzae*, and *A. awamori*. These fungi are well-known producers of lipases, proteases, and amylases and can also enrich the cake so that it can be fully used in animal feed to substitute high cost components [75–77].

Moreover, residues like fruit byproducts, wheat straw, paddy straw, and corn stover may be transformed using SSF enrich their antioxidant properties for animal feed. Most phenolic compounds are mainly present in associated with other molecules, attached to sugar molecules or amines, organic acids, or lipids. This reduces their antioxidant activity. During SSF, lignocellulolytic enzymes (e.g., peroxidase, manganese superoxide, dismutase) and laccase and carbohydrate-cleaving enzymes (e.g., β -glucosidase) are produced. The enzymatic hydrolysis of these phenolic conjugates generates free phenolics (such as gallic, ferulic, and ellagic acids) and low molecular weight lignin molecules with higher antioxidant power [72,78,79]. SSF using several microorganisms has been utilized to increase phenolic contents and antioxidant features of several byproducts [78,79].

Therefore, the SSF process can be used to increase the nutritional value and antioxidant features, and simultaneously add value to waste through the production of biotechnology products, such as possible substitutes for animal feed components with higher digestibility and protein content or enzymes.

2.3. Production of Generic Fermentation Feedstock Medium

A promising alternative for adding value to agro-industrial wastes is their transformation to generic fermentation feedstock medium by SSF. During SSF, the microorganism produces several hydrolytic enzymes (such as endo-exoglucanases, proteases, xylanases, cellulases, and amylases) to hydrolyze most of the available biomacromolecules. Hydrolysis of these macromolecules into monomers produces a nutrient-rich solution containing readily assimilable sugars, (e.g., fructose, glucose and xylose) and many other nutrients (e.g., phosphorus, amino acids, and mineral salts), which are readily metabolized by microorganisms when used as growth-medium for submerged fermentations [80,81]. These hydrolysate products may replace commercial organic supplements utilized in submerged microbial fermentation to produce biopolymers, biofuels, organic acids, and a wide range of other relevant biological metabolites, which makes it unnecessary to add commercial high-value products, e.g., yeast extracts or casein [80,81]. According to Batista et al. [82], in Brazil the sources of nitrogen currently used in culture media are imported and represent about 30%–40% of the final costs of the medium. The replacement of these expensive components (such as casein and peptone) helps minimize the dependence on imports of these components, and at the same time allows the use of agro-industrial residues to produce highly value-added products.

Table 2 presents some examples of products obtained through the use of generic feedstock medium. Cinelli et al. [83] investigated the hydrolysis of starch granules from babassu flour using a multienzyme complex produced by SSF in babassu cake. Hydrolysis of babassu flour yielded a product rich in free amino nitrogen (FAN) and glucose. The SSF process with enzyme extract carried out on a simple batch of babassu flour allowed 83% of the starch of the babassu flour to be converted into ethanol. Du et al. [84] used wheat bran to synthesize protease and glucoamylase via SSF, which were utilized for flour and gluten hydrolysis. The hydrolysate was examined as generic feedstock for fermentative production of succinic acid and around 64 g/L succinic acid was obtained. Botella et al. [85] used partly pearled wheat grains as substrate for the cultivation of *A. awamori*, and the hydrolysate obtained through this system was used to produce ethanol and, more interesting biodegradable plastic PHB (polyhydroxybutyrate). Recently, Dimou et al. [86] purposed a biorefinery concept in which wine lees (a residue from wine industry) were fractionated for the achieving of antioxidants, tartrate, and ethanol, and the residual stream enriched in yeast cells was used as fermentation supplements for PHB production using a strain of *Cupriavidus necator*. The enzymatic hydrolysis of the yeast cells was performed by an enzyme consortia produced by SSF of *Aspergillus oryzae*. The hydrolysate was supplemented with crude glycerol and was employed as renewable resource for the manufacture of PHB. A production of 30.1 g/L of PHB with a productivity of 0.56 g/L·h was attained during fed-batch fermentation using a FAN concentration of 700 mg/L in the hydrolysate and supplementation with trace elements.

Another approach to supply an additional nitrogen carbon source in the generic feedstock medium is to add a step of autolysis fungus into the protocol. The fungal autolysis provides the regeneration of the nutrient components from fungal biomass is mixed with the hydrolysates to generate a nutrient-complete media [80,87]. According to Koutinas et al. [80], autolytic conditions induce the secretion of hydrolytic enzymes by fungi. They hydrolyze cellular constituents and any residual components of the fermentation media, producing a cheap complex nutrient product similar to yeast extract.

This process was used by Wang et al. [88], using rapeseed meal as substrate they produced a product with microbial nutrients similar to yeast extract. The nutritional resemblance between the produced generic feedstock and a combination of commercial peptone and yeast extract was confirmed by growing *Saccharomyces cerevisiae* cells. A production of 162.8 g/L PHB was attained by Xu et al. [87] using wheat-derived media (wheat hydrolysates and fungal autolysates) as culture medium for *Wautersia eutropha* [87]. Tsakona et al. [89] employed enzyme-rich solids, produced via SSF of *A. awamori* in wheat milling by-products, in hydrolysis of flour-rich waste streams. The crude hydrolysates were employed as fermentation media for the growth of the oleaginous yeast *Lipomyces starkeyi*. In this process, liquid residues such as manipuera, crude glycerin, or molasses may also be used to

supplement the generic culture media [90]. The use of a generic media, produced via SSF in rapeseed meal and supplemented with crude glycerol resulted in a 1,3-propanediol concentration of 65.5 g/L, with a productivity almost twice as high as achieved with yeast extract as nutrient [90].

Table 2. Examples of products obtained by using generic feedstock.

Solid Substrate	Microorganism Used to SSF	Feedstock for Hydrolysis	Product	Reference
Babassu cake	<i>A. awamori</i>	Babassu flour	Ethanol	[83]
Wheat bran	<i>A. awamori</i> and <i>A. oryzae</i>	Gluten-free flour and gluten from wheat	Succinic acid	[84]
Pearled whole wheat grains	<i>A. awamori</i>	Pearled whole wheat grains	Polyhydroxybutyrate (PHB) and ethanol	[85]
Wheat milling by-products	<i>A. awamori</i>	Flour-rich waste	Microbial oil	[89]
Rapeseed meal	<i>A. oryzae</i>	Rapessed meal	1,3-propanediol (PDO)	[90]

3. Biocatalysts in Effluent Treatment

Conventional effluent treatment technologies are unable to fully remove all contaminant substances from water. Standard biological treatments can deplete, partially or even completely, several organic substances. However, conventional biological treatments are unable to fully remove all substances from water. The toxicity of various organic compounds can interfere with the proper functioning of these processes, which can result in the discharge of compounds in receiving water bodies.

Typically, wastewater treatment processes are evaluated in terms of global pollution indicators such as Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD). However, as a consequence of increasingly strict regulation by environmental agencies for a removal of specific components of waste water, specificity becomes very relevant. If the inhibitory or toxic contaminants can be specifically degraded, the residual organic material in the waste can be biologically treated, thus reducing the treatment cost. In this case, biocatalysts can be employed to achieve a selective removal of compounds in effluent treatment [91].

Like the conventional biological process, enzymatic treatment may be appropriate for some situations and unsuitable for others. Enzymatic processes may be more suitable for some applications such as: elimination of specific compounds from complex mixtures before to biological treatment; elimination of specific compounds from diluted mixtures, in which the conventional biological treatment is not useful, such as the removal of contaminants from groundwater; polishing of wastewater (industrial or municipal) treated or groundwater in order to fulfill toxicity requirements; treatment of waste produced occasionally or in remote locations (including locations of spills or disposal of uncontrolled wastes); treatment “in-plant” of wastewater with low volume and high concentration at the manufacture site in the production unit. Such treatment can enable the reuse of treated wastewater, facilitate the retrieval of the soluble products, or eliminate contaminants that produce problems when combined with other residues from the industrial plant [92]. On the other hand, the problem of enzymatic treatment is its requirement of high amount of enzyme to give efficient removal because of enzyme inactivation. The use of enzymes will be unsuitable in effluents with high concentration of contaminants that interfere with enzymatic activity. Some researchers have studied the use of additives to suppress enzyme inactivation and to reduce the amount of enzyme needed. Another way of increasing the use of enzymes in these treatments is the enzyme immobilization. Enzyme immobilization may improve usually the biocatalyst operational stability, and prevents the contamination of the solution being treated by the enzyme. Moreover, insolubilized enzymes can be easily recovered from the reaction medium and that way, they may be reused or employed in continuous reactors [93].

The employ of enzyme biocatalysts in waste treatment was first suggested in the mid-1930s. However, the idea of employing biocatalysts to remove specific contaminants in mixed residues was

established after 1970 [94]. Since then, biocatalysts have been used as an alternative to conventional wastewater treatment and have increased the interest of many researchers due to their several advantages including the increase of recalcitrant organic pollutants, which reduces the possibility of carrying out an efficient conventional biological or chemical treatment; recognition of the ability of biocatalysts to act on specific compounds; and the recent advances in biotechnology, which rendered feasible the economical production of biocatalysts [91].

Different mixtures of biocatalysts and degrading microorganisms are produced by companies throughout the world. The mixtures are commonly effective solutions for effluent treatment and odor control in several industrial types. However, as pointed out by Aitken [94], several technical problems must be solved so that enzymatic processes can become technically and economically practicable. The final products must be more biodegradable, with a lower toxicity, and more susceptible to further treatment than the starting material. Most studies consider only the elimination of the contaminant from the solution without considering the toxicity of the generated products. The biocatalysts should act selectively on the desired compounds in a waste combination. The elimination rates of specific pollutants must be compared with controls containing clean water in order to evaluate the likely effects of the medium on enzyme kinetics. The biocatalyst must be stable under typical treatment conditions. The reactors for enzymatic processes should be as simple as the conventional perfectly mixed reactors (if the cost of the enzyme is low enough to ensure its disposal after a residence time) or coupled membrane reactors (in order to recycle the enzyme after each cycle or during the recycling in continuous flow reactors). The choice of a reactor configuration for a particular use should be performed afterward a cautious economic analysis. Finally, the biocatalyst should be relatively stable under treatment conditions.

Enzymes may be used in methods for treating effluents that have a lower environmental aggressivity than the conventional ones. Enzymes are very versatile and very efficient under mild reaction conditions, this is advantageous compared to conventional methods of physical-chemical treatment. The natural origin of enzymes decreases their negative environmental impact, converting the enzymatic treatment of wastewater an environmentally sustainable strategy. The high price of enzymes is the main problem of the use of enzymes, although the advantages of enzymatic treatment of sewage are many. Currently, the treatment of wastewater using enzymes on a large scale is not economically feasible [95].

However, the cost of the enzymatic treatment can be considerably reduced, as suggested by Mugdha and Usha [95], if the maximum capacity to reuse the enzyme is achieved through the use of standard immobilization procedures or through a combination of enzymatic technology with nanotechnology, known as Single Enzyme Nanoparticle (SEN). Laccases immobilized onto silica nanoparticles have been used to remove bisphenol from secondary effluent in a municipal wastewater treatment plant [96] as well as phenol from coking wastewater [97]. There are many studies on the synthesis and comparison of SENs with free enzymes; however, SEN applications for wastewater treatment are still in the rational design phase [98,99]. Other authors, like Demarche et al. [91], suggest that enzymatic technology must be combined with the technologies available for obtaining better results.

Another alternative to reduce costs of the enzymatic treatment is to obtain enzymes from wastes. For example, potato pulp is a residue of the starch industry that contains a high level of peroxidase activity [100]; soybean seed hulls, a soybean-processing industry by-product is a rich source of peroxidases [101]; and oil palm empty fruit bunch (OPEFB) and palm oil mill effluent (POME) to produce lignocellulolytic enzymes [102]. The industrial implementation of enzymes for bioremediation depends on the availability of high amounts of low-cost material containing highly active and stable enzymes.

Biocatalysts can be used to treat several effluents, including wastewater with phenolic contaminants, pesticides, surfactants, heavy metals, and cyanide, residues from pulp and paper industry, food industry residues, in sludge dehydration, bioconversion of crustacean shells, and pectin degradation [91,103]. This review will present some examples of biocatalysts used in the treatment

of effluents rich in fat content (food industries) and removal of color and phenolic compounds (textile industries).

3.1. Use of Biocatalysts in the Treatment of Effluents from Food Industries

Increased productivity from food industries is a worldwide phenomenon and has resulted in an increase of the solid and liquid processing effluents from these industries. The large volumes of effluents, increasingly restrictive environmental legislation, high costs of the treatment, and increased consumer awareness have transformed the treatment of wastes into a main concern in the food industry.

The volumes of wastewater generated per ton of product vary in each sector of the food industry, which are (m^3/t) 2 for cheese production, 1.7 for milk processing, 15 for meat processing, 7 for beer production, and 8 for fish processing [104]. The concentration of the effluent can vary from low (as in washing water of sugar and dairy plants) to high (such as in effluents from the production of cheese, wine, and oil), mainly regarding proteins, organic matter, aromatic compounds, acids, existing nutrients, etc. [105]. Efremenko et al. [106] reported that salts (10%), proteins (0.5%), fats (3.8%), and carbohydrates (1.2%), are the major components of the effluents from food industries. Wastewater from dairy industries, abattoirs, and canning industries, in addition to high volumes, contains high concentrations of fat. Fats hydrolysis is slower than other organic fractions, which cause considerable nuisance in the biological treatment. If fat is not removed properly in a preliminary treatment step, several problems occur in the biological treatment system, including formation of scum, effluent with poor quality, clogging, and creation of preferential ways through the bed of sludge (especially in up flow anaerobic sludge blanket—UASB), development of a floating sludge with low activity and undesirable physical characteristics, biomass washout, and inhibition of acetogenic methanogenic microorganisms because of the accumulation of long chain fatty acids (LCFA). In aerobic bioreactors, these substances reduce the rate of transference of oxygen to the microbial consortium by forming a lipid layer around the floc, which causes problems in the aeration system, facilitates the development of filamentous microorganisms that are implicated in the production of stable foams and scum on the surface of the aeration reactor, and hampers sedimentation. The presence of fats also facilitates the development of agglomerates inside the secondary sludge flocs, promoting disagreeable smells and decreasing the competence of the treatment station. Moreover, the fat adsorption on the surface of the sludge in both aerobic and anaerobic processes may decrease the transport velocity of soluble compounds to the cells and therefore decreases the substrate conversion rate [107–109].

The use of biocatalysts is a treatment alternative for effluents with high levels of fats. Lipases or crude enzyme preparations with significant lipase activity may be used in wastewater treatment to hydrolyze fats, that way dissolving them. This enhances the biological decontamination of wastewaters rich in fats. In enzymatic pretreatment, hydrolysis of triglycerides in fatty acids and glycerol occur, which reduces the diameter of the particles and increases the surface area; thus, facilitating the organic matter degradation by the microbial consortium. This improves the performance of the microbial community in further stages of the waste treatment [110,111].

In several studies, Masse et al. described the use of a commercial pancreatic lipase (PL-250, Genecor International, Palo Alto, CA, USA, EC 3.1.1.3) for hydrolysis of fat particles in slaughterhouse wastewater. Pancreatic lipase 250 is efficient in the hydrolysis of triglycerides containing LCFA with more than 12 carbons, abundant in animal fat. Pretreatment with this lipase decreased the mean particle size and also gave long-chain fatty acids [112]. The effect of the enzymatic hydrolysis of slaughterhouse effluent having 550 mg/L of fat in an anaerobic sequencing batch reactor (ASBR) was studied by Masse et al. [113]. However, the authors did not observe significant differences in the reactor performance by the previous enzymatic hydrolysis step.

Shon et al. [114] isolated a strain of *Pseudomonas* sp., which is a producer of lipase (38.5 U/g DCW using the optimal medium after 9 h), and evaluated its biodegradation potential at 30 °C and pH 8. The authors obtained elimination efficiencies of 62%–94% for different fats. The waste elimination by *Pseudomonas* sp. increased by a 41% comparing with use of the bacteria presented in the

waste. Jeganathan et al. [115] studied the hydrolysis of oils and greases from wastewater of animal feed industry using *Candida rugosa* lipase (Sigma-Aldrich Pvt. Ltd., St. Louis, MO, USA, EC3.1.1.3) immobilized in calcium alginate (890 U/mg at 35 °C for 3 d) and obtained 65% and 69% removal of COD and O&G (oil and grease), respectively. In the bioreactor used as control, these percentages were of 49% and 45%, respectively.

Dors [116] studied the use of commercial pancreatic lipases (Kin Master, Rio Grande do Sul, Brazil and Nuclear, São Paulo, Brazil, EC 3.1.1.3) in the biodegradability of wastewater from poultry abattoir. Enzymatic treatments were performed by varying the enzyme concentrations (0.10% to 0.35% *w/v*). The effluent was biodegraded at 35 °C/100 rpm for 30 d, with a removal of COD obtained 2.3 to 2.9 times greater than that obtained with the raw effluent without enzymatic pretreatment. Mendes et al. [117] investigated effluents from dairy industries, rich in lipids, partially hydrolyzed with a commercial porcine pancreatic lipase (Nuclear, São Paulo, Brazil, 1.77 U/mg) and obtained better results when the hydrolysis and degradation were carried out simultaneously using a low enzyme concentration (0.05% *w/v*).

It is important to remark out that all the aforementioned studies used pure cultures or commercial enzyme preparations containing several compounds as preservatives and stabilizers, which can negatively influence the microbial metabolism. Moreover, these commercial enzymatic preparations present high costs, which make the enzymatic pretreatment procedure economically infeasible on an industrial scale. Therefore, the utilization of cheap enzymes is a key point in wastewater treatment.

The Laboratories of Microbial Biotechnology (LabiM) and Environmental Technology (LTA) at the Federal University of Rio de Janeiro (UFRJ) have been carrying out, since 2001, joint work on production of hydrolytic enzymes by solid state fermentation (SSF) by using filamentous fungi (*Penicillium* sp, *P. brevicompactum*, and *P. simplicissimum*) isolated from agro-industrial wastes and application of microbial enzymatic preparations for pretreatment of wastewater with high fat content. The coupled use of enzymatic hydrolysis and aerobic or anaerobic microbiological processes for the treatment of effluents from fish-processing, poultry abattoir, and dairy industries, containing different initial O&G contents (700–2400 mg/L) yielded good results that led to its study in a pilot or even industrial scale. The COD elimination efficiencies for pretreated effluents (80%–97%) were over those obtained for effluents without enzymatic pretreatment at several O&G concentrations. All these studies were conducted with lipase-rich enzyme preparations (and therefore characterized in terms of lipase activity) in the hydrolysis step and with mixed microbial populations (sludge from treatment plants) in the biodegradability assays.

A scheme showing the steps of O&G transformation in the treatment of effluents is shown in Figure 2. In conventional biological processes, O&G are adsorbed onto sludge flocs, and microorganisms produce lipases and other extracellular enzymes to hydrolyze the contaminants, for instance triacylglycerols are hydrolyzed to free fatty acids and glycerol, which are consumed by microorganisms after being captured by the microbial cells. Because the lipid feed rate is higher than the speed of lipid hydrolysis and consumption, lipid accumulation occurs in sludge flocs and effluent. In the combined enzymatic and biological processes, a step of enzymatic pre-hydrolysis (with solid enzymatic preparations produced by solid-state fermentation of agro-industrial wastes) converts triacylglycerols to fatty acids and glycerol, which are then fed to bioreactors. As a result, the microorganisms rapidly consume the substrate introduced into the reactors, with no accumulation of triacylglycerols and operational problems resulting from this accumulation.

The coupled employment of enzymes manufactured by this research group on the anaerobic treatment of effluents containing a high-fat content directed to higher and more specific production of methane (until 216 mL CH₄/g COD removed) when compared to the raw effluents. In addition, no operational problem was found in the reactors fed with enzymes during the whole operation time, whereas in the control reactors there were recurrent cases of obstruction of the effluent and biogas outputs. This led to the necessity of regular cleaning of the three-phase separators, required for the proper performance of flow anaerobic sludge blanket (UASB) reactors. Both the quantity of scum

produced and the fat concentration in the scum and biomass in diverse sludge fractions were clearly higher in the control reactors, revealing the relevance of the enzymatic pretreatment [110].

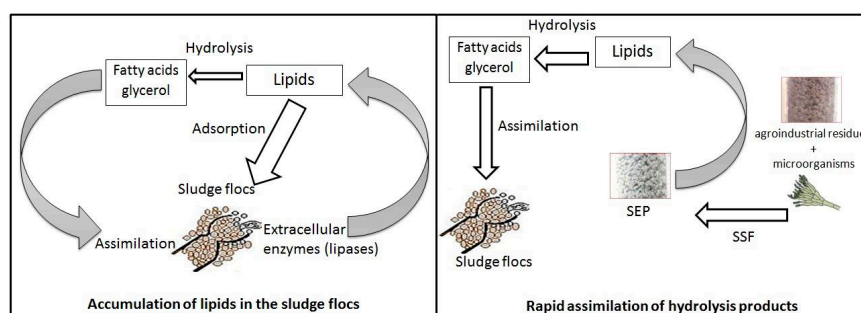


Figure 2. Steps of oil and grease (O&G) transformation in the conventional biological processes and in the combined enzymatic and biological processes.

Our research group also evaluated the coupled use of enzymes and biosurfactants in the processing of wastewater [118,119]. This is a new approach, because the use of biosurfactant had only been reported to increase the hydrolytic activity of lipase [120], cellulases [121], and bacteria that exhibit lipase and biosurfactant activities [122]. Therefore, both processes facilitate biodegradation by increasing the fraction of soluble organic matter in the effluent. Another approach carried out by the research group was the combination of enzymatic pre-hydrolysis and anaerobic biological treatment in thermophilic and mesophilic conditions.

In the work of Duarte et al. [123], different combined treatments were evaluated in wastewater from the fish processing industry using solid enzymatic samples (SEP) achieved by solid state fermentation of *Penicillium simplicissim*. SEP contained average lipase activity of 62 U/g. The best outcomes were achieved with a mixed processing (hydrolysis at 50 °C and anaerobic processing at 30 °C). The hydrolysis at high temperature decreased the demands of required enzyme, the hydrolysis time and the cost and time of the mesophilic anaerobic treatment, which suggest the interest of this process at industrial level.

The results presented show that an enzymatic pretreatment or the direct addition of enzymes in the bioreactors can improve the treatment of effluents from food industries containing high percentage of fats, including better treatment of effluent, with lower concentrations of organic matter, suspended solids and turbidity; reduction of operational problems such as clogging in feed and discharge effluents pipes as well as in collectors of biogas; and less production of scum in anaerobic reactors. Moreover, the use of biocatalysts in treatment of effluents can reduce the costs for treatment and disposal of the waste, because the fat separated into flotation units can be followed by biological treatment after enzymatic hydrolysis and can increase the methane production in anaerobic processes, due to exploration of the methane potential of the fat presented in the effluent.

In the applications cited, it may be necessary, depending on the source of the effluent, to adjust the pH and maintain the temperature at suitable values during the reaction time with the biocatalysts. Such conditions would also be required in a conventional biological treatment. Other precautions, such as the removal of inhibitors or even the addition of cofactors, are not required to conduct the enzymatic pretreatment because the lipases and proteases constituting the employed enzyme preparations only require pH and temperature adjustment. At the same time, effluents from food industries do not contain compounds that inhibit enzymatic activity. Thus, the complexity of the enzymatic pre-treatment followed by a biological treatment would be similar to that of a conventional biological treatment, and the cost would be heavily dependent on the cost of the biocatalysts. Thus, it is important that the production of biocatalysts is conducted more cheaply, like SSF in agro-industrial residues.

3.2. Application of Biocatalysts on Color Removal of Effluents

Wastewater generated in textile industries is considered difficult to treat because they present aromatic and complex and stable heterocyclic colorants that are not readily responsive to biological treatment. The mineralization of organic compounds, dyes, and the decrease of the harmfulness of the wastewater produced by fabric industry is a challenge and an ecological worry. Colored water produces a reduction of light availability, which is indispensable for the growth of the aquatic organisms. However, currently wastewater treatment processes for the mineralization of dyes are studied more than technologies for color removal [124].

Most of the tints used in textile factories are azo compounds, i.e., molecules with one or more azo bonds ($-N=N-$) attaching aromatic moieties. The versatility of this class is due to the ease with which they can synthesize azo compounds and the fact that they have good fixing and affordable characteristics [125,126]. However, these dyes are recalcitrant xenobiotic compounds because they have an $N=N$ bond, and also due to the fact that they may contain other groups that are not readily biodegradable, for example, sulfonic acid groups (SO_3H). Besides being considered toxic, their environmental impact is increased by the formation of aromatic amines (anilines) considered to have carcinogenic and/or mutagenic impacts caused by the reductive azo bond breakage [127].

Among the conventional physicochemical processes used for color removal wastewater, the following can be highlighted: cavitation, coagulation/flocculation, adsorption, oxidation, membrane separations and ion exchange. Bearing in mind that a relevant percentage of the organic material of textile wastewater is biodegradable, anoxic, aerobic, and anaerobic biological treatments and their mixtures have been successfully employed in the processing of textile wastewaters. Recently, new individual or coupled processes have been analyzed to treat textile wastewaters. These processes are membrane separation (single or combined with biological processes—as membrane bioreactors), photochemical, ultrasonic, and electrochemical methodologies. The chemical, physical and biological treatments have benefits and disadvantages, such as economic limits, low efficacy, formation of toxic products and production of toxic sludge. In order to overcome such limitations and to achieve adequate levels of color removal, more recent studies have evaluated combinations of two or more processes. New adsorbent or coagulants and better treatments such as sonooxidation, electrocoagulation-electrooxidation or photo oxidation are gaining interest in the processing of fabric wastewaters [128].

Solís et al. [126] presented an excellent survey of different microorganisms tested for decolorization and mineralization of azo dyes, comprising yeasts, algae, bacteria and filamentous fungi. Saratale et al. [125], however, showed that the disadvantages of employing pure cultures of filamentous fungi (the most widely studied for dyes degradation) are very long cultivation cycles, the necessity for nitrogen-limiting environments, high hydraulic retention time for full decolorization, and the difficulty of preserving fungi in bioreactors.

The use of enzyme extract has significant benefits compared to direct use of microorganisms. Commercially, the enzymatic extracts are easily standardized to allow precise dosing. The implementation is easy and can be readily altered following the characteristics of the dyes to be eliminated [129]. Two groups of oxidoreductase enzymes have been very investigated for wastewater color removal, polyphenol oxidases and peroxidases. A search of the literature reveals many laboratory-scale researches on the degradation of dyes with biocatalysts [91,126]. However, these studies are conducted with synthetic solutions of a single dye in water, in other words, in the absence of interference and inhibitors normally present in industrial effluents. It is essential to evaluate the decolorization of real industrial effluents, which are complex systems with strong coloration, fluctuating pH, high temperatures, and large amounts of suspended solids, dissolved salts, and COD [130]. Considering the limited number of studies with real effluents and field applications, the color removal in real industrial effluents by biocatalysts from different biological sources is showed in Table 3. The data presented in Table 3 show that systems based on soluble or immobilized biocatalysts can be effective in the processing of recalcitrant wastewater containing colorants from textile factories, dyeing and stamping.

Table 3. Color removal from industrial effluents by biocatalysts of different biological sources.

Enzyme/Source	Effluent/Treatment Conditions	Decolorization	Reference
Bitter gourd (<i>Momordica charantia</i>) peroxidases (BGP—99 U/mg protein)—immobilized on concanavalin A layered calcium alginate—starch beads	Textile effluent (diluted) Continuous two-reactor system—first column with immobilized BGP (1162 U) and second column with activated silica, 1.0 mmol/L hydroxybenzotriazole, 0.72 mmol/L H ₂ O ₂ , 16 mL/h, pH 5.0, 37 °C, 2 months	<ul style="list-style-type: none"> 90% during initial 10 d of operation decolorization was gradually decreased 40% after 60 d 	[131]
Bitter gourd (<i>Momordica charantia</i>) peroxidases (BGP—99 U/mg protein)—soluble and immobilized on Sephadex G-50	Dyeing effluent, 0.125 U/mL, pH 3.5, 0.75 mmol/L H ₂ O ₂ , 30 °C, stirring, 8 h	<ul style="list-style-type: none"> 48% with soluble BGP 95% with immobilized PPO 	[132]
Crude enzyme produced by a marine white-rot fungus (921 U/L laccase)	Textile and paper and pulp industry effluents, 9 U/mL laccase, pH 6, 60 °C, 6–12 h	<ul style="list-style-type: none"> 11% for textile effluent A (10%) after 12 h 22% for textile effluent B (10%) after 12 h 71% for black liquor (10%) after 6 h 	[133]
Horseradish peroxidase (HRP) immobilized on β -cyclodextrin-chitosan complex (3500 U/g)	Textile effluent (diluted 1:20) Continuous bed reactors filled with the un-crosslinked or crosslinked HRP (4200 U each), 20 mL/h, 0.6 mmol/L H ₂ O ₂ , 50 °C	<ul style="list-style-type: none"> 100% until the 10th day of run with un-crosslinked HRP system 100% for up to 20 days of run with crosslinked HRP system 	[134]
Laccase from <i>Trametes trogii</i>	Textile factory effluent (20%), laccase with or without a mediator (1-hydroxybenzotriazole—HBT, pH 5, 30 °C)	<ul style="list-style-type: none"> 10% after 9 h using 9 U/mL laccase 81%, 70%, 65%, and 58% after 6 h with laccase—HBT system (5 U/mL; 3 mmol/L) and 5%, 10%, 20%, and 30% effluent 	[135]
Laccase (2.35 U/mg protein) produced by basidiomycete fungus <i>Cyathus bulleri</i>	Dyeing bath effluent, pH 9, 0.15 g/L alum, coagulated dye reconstituted in phosphate buffer (pH 5.6). 2-2' azinobis (3-ethylbenzthiazoline-6-sulfonate (ABTS)) 100 μ mol/L and laccase (10 U/L), Enzyme membrane reactor 1 L (polyacrylonitrile membrane of 20 kDa), HRT 10 h	<ul style="list-style-type: none"> 85% for 14 d after initial drop in laccase activity (by 40%), it was stably maintained at 50% up to 14 d membrane fouling and sludge formation were avoided nearly 60% ABTS was recovered from permeate 	[136]
Laccase and peroxidases Baysolex (an enzymatic cocktail containing laccase, catechol oxidase), bilirubin oxidase and peroxidase from Bayer	Wastewater from the dyeing process of the textile company containing Reactive Black 5, Reactive Red 158, and Reactive Yellow 27. Stirred-tank 1 m ³ , pH 6.4, addition of hydrogen peroxide and a redox mediator, 42 °C, 20 min	<ul style="list-style-type: none"> 91%, 78%, and 17%, for the Reactive Black 5, Reactive Red 158, and Reactive Yellow 27, respectively 	[137]
Potato (<i>Solanum tuberosum</i>) polyphenol oxidase	Textile dyeing industry, 424 U/mL, pH 3.0, 25 °C, 1 h	<ul style="list-style-type: none"> Decolorization was analyzed with Vis Spectroscopy. After treatment, a remarkable diminution in absorbance peaks in whole visible region was observed 	[138]
Potato polyphenol oxidase (PPO)—soluble and immobilized on Celite 545	Dyeing effluent, 1.5 U/mL, pH 3, 37 °C, stirring/1 h	<ul style="list-style-type: none"> 82% with soluble potato PPO 95% with immobilized PPO 	[139]
Salt-tolerant laccase from <i>Peniophora cinerea</i>	Textile industry effluent (diluted 1:10), pH 4.0, 1.0 U/mL pre-purified laccase, 1 mmol/L syringaldehyde, 1 mmol/L MnSO ₄ , 1 mmol/L sodium oxalate, 50 °C, 72 h	<ul style="list-style-type: none"> 54.6% 	[140]
Horseradish peroxidase (HRP) from Horseradish (<i>Armoracia rusticana</i>)	Simulated textile wastewater containing (120 mL/L) Drimarene Blue X-3LR (DMBLR), Drimarene Blue X-BLN (DMBBLN), Drimarene Rubinol X-3LR (DMR), and Drimarene Blue CL-R (RBBR); 35 °C, 0.55 mmol/L and 1 h	Color removal for DMBLR (99%), DMBBLN (77%), DMR (94%), and RBBR (97%).	[141]
Commercial laccase from <i>Aspergillus oryzae</i> and a laccase rich extract from <i>Pleurotus ostreatus</i>	Drimaren Blue X-3LR (DMBLR), Drimaren Blue X-BLN (DMBBLN), Drimaren Rubinol X-3LR (DMR), and Drimaren Blue C-R (RBBR); 0.02 U/mL, 0.017 mM of ABTS, 35 °C and pH 4	Decolorization of DMR (80%–90%, 1 h) and RBBR (80%–90%, 24 h) with both laccases (presence of ABTS). DMBLR (85%–97%, 1 h) and DMBBLN (63%–84%, 24 h) with both laccases (absence of ABTS)	[142]
Lignin peroxidase from <i>Phanerochaete chrysosporium</i>	Methylene blue (MB) 50 mg/L, 30 °C, pH 4, 30 min, ratio MB:H ₂ O ₂ of 1:5	Efficient removal of 90% color in reactions with MB	[143]

3.3. Application of Biocatalysts in the Elimination of Phenolic Compounds

Phenols and related compounds contaminate wastewater of many industries, for example those from the pulp and paper sectors, as well as olive oil, coal, plastics, pharmaceuticals resin manufacturing, oil refineries, coking operations, and paint [144].

The industries producing olive oil are responsible for the annual generation of 30 million m³ of wastewater in the Mediterranean region (Greece, Tunisia, Spain, Italy and Portugal) during the period of olive oil production [105]. Olive-mill wastewater (OMW) is an obscure stained emulsified effluent with a large diversity of composition, depending on various parameters such as the variety, maturity, and region of origin of the olives and especially the technology used for oil extraction. OMW is commonly characterized by elevated salt content, low pH value and great organic load with high concentrations of carbohydrates, polysaccharides, fatty acids, tannins pectins, polyalcohols, and phenolic compounds (mainly polyphenols). This great variety of compounds, many with contaminating, phytotoxic and antimicrobial features, converts OMW into a very dangerous waste for humanity and the environment, and its discard into waterways is a very relevant environmental problem in all producing countries. Pollution of ground and surface waters, soil contamination, odor nuisance, environmental degradation, as well as, effects of toxicity and growth inhibition on species from different trophic levels have been reported [145,146].

Malaysia produce 39% of the worldwide production of palm oil, producing significant quantities of contaminated wastewater, called palm oil mill effluent (POME). In coffee farming areas, such as Vietnam, Brazil or Colombia, the wastewater formed by this process is a major ecological danger. Thus, the development of cheap technologies for the processing of this wastewater has become an urgent matter [105,147–149].

The enzymes used to eliminate phenolic compounds from the effluents include polyphenol oxidases (laccases and tyrosinases) and peroxidases (lignin peroxidase, horseradish peroxidase and manganese peroxidase). These enzymes can catalyze the oxidation of phenolic compounds such as phenols or chlorophenols, bisphenol A and phenolic endocrine disrupting compounds [93].

Studies about removal of these compounds are frequently conducted with aqueous solutions. According to Demarche et al. [91], systems designed for synthetic effluents may be transferable to the processing of industrial effluents rich in phenol. However, the use of more complex matrices, which simulate industrial effluents, must be considered in laboratory experiments. Table 4 shows the results obtained in direct application of biocatalysts for removal of phenolic compounds in industrial effluents.

Table 4. Removal of phenolic compounds from industrial effluents by biocatalysts of different biological sources.

Enzyme/Source	Effluent/Treatment Conditions	Results	Reference
Crude extract of soybean peroxidase (SBP)	Coal-tar effluent containing phenols (15 mmol/L), SBP, peroxide, and polyethylene glycol (PEG), sodium dodecyl sulfate (SDS) or Triton X-100	<ul style="list-style-type: none"> • Step additions of both SBP and hydrogen peroxide reduced the SBP concentration • Triton was more effective for $\geq 95\%$ removal of 1 mmol/L phenol 	[150]
<i>Horseradish peroxidase</i> and catalase from Sigma	Phenol-containing (10–14 mg/L) condensates from the scrubber of a recovery furnace from hardwood Kraft pulp and paper mill, pH 7.0, HRP, 0.70 mmol/L H ₂ O ₂	<ul style="list-style-type: none"> • Reduction of total phenols to <1.0 mg/L with 0.3–1.0 U/mL HRP • Reduction of total phenols to <0.5 mg/L with 0.8–4.0 U/mL HRP 	[151]
Laccase from <i>Lentinula edodes</i> immobilized on Eupergit® C (170 U/g)	Olive mill wastewater containing 1.35 g total Phenols/L and 0.89 g <i>o</i> -diphenols/L, fluidized bed reactor with 2.7 g Eupergit-laccase complex, effluent volume: catalyst weight ratio of 200, OMW 5 mL/min, 35 °C, recirculation for 2 h	<ul style="list-style-type: none"> • 55% to 70% of total phenol removal • 64% to 88% of <i>o</i>-diphenol removal • Negligible total phenol removal in the absence of laccase • OMW (200 mL) with 5, 10, and 50 U soluble laccase led to 42%, 65%, and 78% of total phenol removal 	[152]
Laccase from the Japanese lacquer tree <i>R. vernicifera</i> (Sigma–Aldrich)	Olive mills wastewaters containing 3.2 (C1) and 5.8 g total phenols/L (C2) and organic extracted fractions (EC1 and EC2), 100 U laccase, 2.5 or 5.0 mg/mL birnessite (δ -MnO ₂), pH 5.0, 30 °C, stirring, 24–48 h	<ul style="list-style-type: none"> • 25% transformation of the total phenolic content of EC1 (2.5 mg/mL birnessite 48 h) • 60% transformation of the total phenolic content of EC1 (5 mg/mL birnessite, 24 h), it remained practically constant after 48 h • 17% transformation of the total phenolic content of EC2 (5 mg/ml birnessite, 48 h) 	[153]
Soybean peroxidase (SBP)	Alkyd resin manufacturing effluent containing TOC (>40 g/L) and phenol (6.8–27.7 mmol/L), pH 7.0, Triton X-100, enzyme, hydrogen peroxide (peroxide/phenol molar ratio of 1.5), 2 h	<ul style="list-style-type: none"> • 67% removal of 6.8 mmol/L phenol (0.64 U/mL SBP, 450–500 mg/L Triton X-100) • >99% removal of 12.5 mmol/L phenol (1.65 U/mL SBP, 800 mg/L Triton X-100) 	[154]
Soybean peroxidase (SBP)	Oil refinery effluent, SBP, polyethylene glycol (PEG), pH 6.0–8.0, 3 h	<ul style="list-style-type: none"> • in synthetic samples in tap water—$\geq 95\%$ removal of 1.0 mmol/L phenol with 0.12 and 1.5 U/mL of laccase and SBP • In refinery samples—comparable removals required 1.2 to 1.8-fold more enzyme than in synthetic tap water samples 	[155]
Plant peroxidase from potato pulp	Wastewater from fine mechanics industry, potato pulp, hydrogen peroxide, pH 4.0–8.0, 2 h	<ul style="list-style-type: none"> • >90% removal with 2.59 mM H₂O₂, for phenol in the range 0.02–0.1 mM • phenol removal efficiency decreased sharply at pH 10 	[100]
Soybean hull peroxidase (SBP)	Coffee processing wastewater, 218 mg/L total phenols, free and immobilized SBP (crosslinked chitosan beads), hydrogen peroxide 3 mM, pH 6, 45–90 min	<ul style="list-style-type: none"> • Free enzyme (31 U/mL)—19.4% total phenol removal • Immobilized enzyme—32.7% total phenol removal 	[101]

4. Biofuels and Energy

Conversion of lignocellulose biomass into new products agrees with the rules of green chemistry, such as the employment of renewable substrates, energy reduction, and synthesis of commodities in an ecologically friendly way. Such tactic includes new compounds for industrial utilization, cleaner-burning combustibles, and new animal feedstuffs [156].

According to Bozell and Petersen [8], research on fuel tends to study a wide range of different strategies to obtain a specific product or a small number of compounds. In other words, biofuel research is a convergent technology. The choice of the technology to be used is driven by the product identification. The opposite is observed for chemical products, due to the large number of possible products in a biorefinery idea. For synthesis of chemicals, the choice of technology guides the product identification, which explains the complex challenge for the chemical sector in the next few years. Therefore, chemical industry diversification and renewable products are the only sustainable choice. For this reason, efforts should be made to establish a new pattern of chemical production.

The increasing request for liquid fuels motivates the progress of second-generation technologies. Within this context, it is crucial to develop and improve technologies for the elaboration of renewable combustibles, for example diesel, butanol, ethanol and methanol. Biogas should not be neglected due to its importance for heating and cooking. Considering that renewable feedstocks include different substrates, like vegetable oils, starch, sugars and lignocellulose, their use for the production of different fuels is expected both by chemical, thermochemical, or biochemical routes [9]. However, this section will only cover biochemical routes for the elaboration of biodiesel, lignocellulose ethanol, hydrogen and methane.

4.1. Biodiesel

Industrial methodologies used for biodiesel elaboration, which utilizes homogeneous alkaline transesterification of comestible oils or animal fat with methanol, has high ester yields (>95%) in short reaction times [157,158]. However, this route has some drawbacks, such as production of a high quantity of highly alkaline wastewater and difficulty of catalyst recovery. Moreover, the high-price/high-quality raw materials (acidity less than 0.5%) required in such process is economically inconvenient, hindering for biodiesel to economically compete with petro-diesel [157–159]. Lipases (glycerol ester hydrolase, EC 3.1.1.3) are alternative biocatalysts that can be used to overcome the drawbacks related with the currently homogeneous alkaline transesterification route [158]. Most of works on enzymatic biodiesel conversion are carried out using commercial immobilized lipases. However, the high cost of the commercial preparations available on the market limits its application on biodiesel production. In this context, the manufacturing of lipases by SSF is an interesting approach to decrease the enzyme price and may be used to make commodities like biodiesel, which is achieved by a more price competitive enzymatic route. After fermentation, the biocatalyst can be extracted from the solid medium for further use or, as reported recently, the biodiesel synthesis reactions can be performed by the direct addition of the fermented solid into the reaction medium [160–164]. Recently, Aguiéiras et al. [165] studied a two enzyme hydroesterification strategy to synthesize biodiesel employing cheap biocatalysts in both reactions. As a first step, the hydrolysis of macauba oil catalyzed by lipase from dormant castor seed was performed. Then, the esterification of ethanol and the produced free fatty acids catalyzed by fermented *Rhizomucor miehei* babassu cake with lipase activity was carried out. A conversion of 91% at 8 h was achieved and the produced biodiesel features fit relevant Brazilian standards for combustibles (Table 5). A conversion of 92% of esterification was obtained by Soares et al. [160] in 31 h employing fermented solids as biocatalysts in a packed-bed reactor with recirculation. The authors observed that the reaction medium was partially adsorbed by the fermented solid, which was confirmed in a following work [166]. According to Soares et al. [166], during the esterification reactions (48 h), around 20%–30% of the total mass of the reaction medium was adsorbed on the biocatalyst (the dried fermented solid), mainly hydrophilic water and ethanol. This is important because ethanol produces inactivation and competitive inhibition

of lipases. These results are useful for better understanding of the reactions using solid fermented as biocatalysts because, as shown in this review, there are few studies on this subject.

Table 5. Biodiesel production using reactions with fermented solids as biocatalyst.

Solid Substrate	Microorganism	Oil	Conversion (%) and Time (h)	Reference
Corn bran	<i>Burkholderia cepacia</i>	Oleic acid	94%/18 h	[161]
Sugarcane bagasse and sunflower seed meal	<i>Burkholderia cepacia</i>	Soybean oil	95%/46 h	[162]
Sugarcane bagasse and sunflower seed Cake	<i>Burkholderia cenocepacia</i>	Soybean oil	86%/96 h	[163]
Sugarcane bagasse and sunflower seed meal	<i>Burkholderia cepacia</i>	FFAs from hydrolysis of soybean soapstock acid oil	93%/31 h	[160]
Babassu cake	<i>Rhizomucor miehei</i>	FFAs from hydrolysis of macauba oil	91%/8 h	[165]

Although microbial lipases are the most extensively used enzymes for industrial processes, in recent years, vegetable lipases have also attracted researchers' attention. Plant lipases are cheap, may be easily purified, are widespread in environment and exhibited high hydrolytic activity [167]. Due to their high hydrolytic activity, plant lipases can be used as biocatalysts for production of free fatty acids (FFAs) from different sources. The FFAs produced can be esterified with ethanol or methanol to produce biodiesel by hydroesterification route. Acetone powders are insoluble residues obtained by extraction of oilseed homogenates with cold acetone and have been described as effective for hydrolysis of vegetable oils [165,168,169]. Sousa et al. [169] presented good results with acetone powder with lipolytic activity from vegetal seeds. Several oils were hydrolyzed by the enzyme extract obtained from germinated physic nut seeds from *Jatropha curcas*. The obtained free fatty acids were utilized for biodiesel production. For example, full hydrolysis of physic nut oil was obtained using with that biocatalyst (50% (v/v) and 2.5% (m/v)), in the absence of any detergent or organic solvent. The hydrolytic ability of the "acid" lipase obtained from dormant castor seed to hydrolyze triglycerides with different fatty acids chains makes it an attractive biocatalyst for use in the hydrolysis of several raw materials. The hydrolytic potential of this enzyme was observed by Cavalcanti et al. [168], who obtained an acetone powder with activity of 429 U/g. In a work by Aguiéiras et al. [165], this acid lipase produced 99.6% FFAs after 6 h in hydrolysis reaction of acid oil from macauba (*Acrocomia aculeata*) in a medium containing 50% (v/v) oil, low amount of lipase and in just aqueous medium.

4.2. Lignocellulose Ethanol

The world request for liquid biocombustibles was multiplied by more than three between 2000 and 2007, clearly indicating the growing tendency towards the utilization of combustibles produced from vegetable feed stock [170,171]. According to the IRENA (International Renewable Energy Agency) [172] projections, renewable energy could account for 36% of the global energy matrix in 2030. This means to double the global renewable energy portion compared to 2010 levels [172].

Lignocellulose biomass is composed of lignin (a very high molecular weight and cross-linked aromatic polymer), hemicellulose (a highly branched sugar heteropolymer) and cellulose (a linear glucose polymer) [173,174]. The enzymatic hydrolysis, using cellulases, has advantages because the minimal substrate modification (produced in the acid-based route), the superior conversion efficacy and the use of more environmentally friendly physic-chemical operating conditions [9]. Lignocellulose conversion into ethanol follows, at least, four steps: pretreatment, hydrolysis, fermentation, and distillation. If the technological option includes in-house enzyme production, an additional step for preparation of the enzyme blends should also be considered. Different technological approaches have focused on these aspects, such as SSCF (simultaneous saccharification and co-fermentation), SSF (simultaneous saccharification fermentation), SHF (separated hydrolysis fermentation), and CBP (consolidated bioprocess). Regarding the first and second options, after lignocellulose pretreatment, the resulting material could be and fermented, either separately or not, respectively. SSCF also includes

C5 and C6 fermentation. In the case of CBP, a single and modified microorganism would be able to perform all the following steps after pretreatment [175]. It is important to emphasize that, in all given examples, previous biomass pretreatment is necessary in order to provide enzyme access to the vegetal fiber. Moreover, several pretreatment technologies have been studied, including ammonia fiber expansion, steam explosion, soaking in aqueous ammonia, ozonolysis, organosolv, liquid hot water, sodium hydroxide/lime pretreatments, dilute acid, and ionic liquids [176,177]. The option for the technology in each step should be evaluated considering the overall process of production and the destination of each fraction of lignocellulose material.

Ferreira-Leitão et al. [178] studied the steam preprocessing of leaves and sugar cane bagasse by employing CO₂ and SO₂. The highest glucose yield (86.6%) was achieved after pretreatment at 205 °C for 15 min using sugar cane bagasse. The highest glucose yield (97.2%) was achieved after pretreatment at 220 °C for 5 min employing sugar cane leaves. SO₂ replacement by CO₂ is an interesting strategy due to the release of CO₂ during the fermentation process. The pretreatment employing impregnation with SO₂ and performed at 190 °C for 5 min, gave glucose yields of 79.7% (bagasse) and 91.9% (leaves). Moutta et al. [179] analyzed the production of monosaccharides (C5 and C6) from sugarcane, treating straw, bagasse or mixtures of both substrates (bagasse:straw 3:1, 1:1 and 1:3). Samples were preprocessed with sulfuric acid, enabling 90% of hemicellulose solubilization, (58 g/L of xylose). Preprocessed straw was more liable to enzymatic hydrolysis when compared with bagasse, permitting to reach higher the yields of glucose (76% and 65%, respectively), whereas the mixtures of both substrates yielded intermediate yields. Authors suggested that the use of bagasse-straw mixtures in suitable ratios following the market demands or biomass availability may permit the balance of sugarcane biomass obtainability and second generation ethanol (2 G ethanol) elaboration. Similar studies were also performed with hydrothermal pretreatment. Moutta et al. [180] submitted straw, sugarcane bagasse and a bagasse-straw mixture (1:1) to hydrothermal preprocessing at 195 °C for 10 min. An increase hemicellulose extraction from straw (93.3%) compared with bagasse (83.7%), and the obtained hemicellulose from straw contained a higher concentration of inhibitors was achieved by this treatment. Values in between for hemicellulose extraction (88.5%) and inhibitor production were detected for the bagasse-straw mixture. Enzymatic hydrolysis of cellulose under soft reaction conditions (pressure, temperature, and pH) into glucose is highly selective and specific [173]. These conditions are valuable considering savings in energy consumption and decreases in environmental impact. Nevertheless, the price of biomass enzymatic hydrolysis is still excessive [180]. Enzymatic hydrolysis of lignocellulosic biomass has been carried out using an enzymatic complex mixture consisting of three classes of enzymes. Endo-1,4-β-D-glucanases (EC 3.2.1.4) hydrolyze inner β-1,4-glucosidic attachments in the cellulose polymer, very likely attacking the disordered or amorphous areas of the polymer. Exo-1,4-β-D-glucanases, also named cellobiohydrolases (EC 3.2.1.91), release cellobiose disaccharide from the terminal ends of cellulose polymer. Final hydrolysis to glucose is catalyzed by 1,4-β-D-glucosidases (EC 3.2.1.21), which hydrolyze cellobiose and also can release glucose molecules from some soluble cellooligosaccharides [181,182].

Significant advances in this area have been made in recent years in several process steps: pretreatment, hydrolysis, and fermentation. In addition, significant progress has been achieved in optimizing the elaboration of enzymes and evolution of micro-organisms that ferment C5 and C6 [183–186]. Thus, some industrial initiatives have been observed worldwide. In Brazil, the technologies for 2 G ethanol production are coming out of the experimental stage and reaching a commercial scale. Recently, two commercial-scale plants were installed in Brazil. The production of 2 G ethanol in an factory began in the Southern hemisphere on a commercial scale by GranBio, a 100% Brazilian industrial biotechnology company. Bioflex 1, a factory constructed in Alagoas, is able to produce 82 million liters of 2 G ethanol per year. The plant uses the technology pretreatment PROESA[®] of the Italian company BetaRenewables (Company Group M&G, Strada Ribrocca, 11-15057, Tortona (AL), Italy), the enzymes of the Danish Novozymes, and yeast of the Dutch DSM. [187]. Raizen recently presented its plant for 2 G ethanol, installed in the state of São Paulo, can produce 40 million liters of ethanol per year. The company has a partnership with the Danish company Novozymes

for development of enzyme technology for the 2 G ethanol production [188]. Raizen, in partnership with Logen Corporation, a Canadian biotechnology company, maintains a cellulosic ethanol plant for tests in Ottawa, Canada. The objective is to acquire all the expertise needed to develop the Raizen business unit in Brazil. Together, Raizen and Logen Corporation formed Logen Energy, owner of the production technology of second generation ethanol [189]. The first U.S. commercial-scale plant was an initiative of the “Project Liberty” in Iowa, a coupled venture of POET and Royal DSM. It plans to manufacture 20 million gallons of 2 G ethanol per year, utilizing 770 tons of corn cobs, stalks, and husks per day [190]. Abengoa, a Spanish renewable energy giant company, opened a factory in Hugoton, Kansas, aiming to synthesize 25 million gallons of ethanol per year, using 1000 tons daily of wheat straw and corn stoves, together to dedicated feedstocks such as prairie grasses and switchgrass [191]. There is also the chemical giant DuPont’s factory located in Nevada, Iowa, that intend to produce 30 million gallons annually. The facility will also use corn stover residues, a nonfood feedstock that consists of corn stalks and leaves. These three US plants together are scheduled to produce around 80 million gallons of 2 G ethanol each year.

4.3. Methane

An overview of different technologies available for wastewater treatment shows that anaerobic technology is increasingly recommended as the best alternative because of its advantages: low power consumption, low requirement for nutrients, small sludge production, large efficiency in the reduction of organic load, and generation of biogas with high calorific value.

The configuration of anaerobic bioreactors has been improved so that technical problems (such as long retention time) can be overcome, resulting in growing technical feasibility for anaerobic technology, especially in the treatment of effluents containing high biodegradable organic loads. This has the advantage of obtaining products with high added value (for example hydrogen and/or methane) which can reduce treatment costs [105].

Treatment of waste generated in the processing of different foods (beverages, apple juice, milk, yogurt, beef) can lead to methane yields between 202–549 Nm³ CH₄/ton VS applied to the methane content in the biogas of 58% to 76% [192]. Labatut et al. [193] summarized the mean specific methane yield (SMY) of various substrates in their research. Substrates with a high lipid content and easily-degradable sugars (e.g., ice cream and used oil—502.3 and 648.5 mL CH₄/g VS added, respectively) have the highest SMY, while lignocellulosic substrates, such as switchgrass (122.2 mL CH₄/g VS added) have low values SMY. Thus, the anaerobic microorganisms can hydrolyze from substances of low molecular weight, almost instantly (i.e., sugars), to even more complex substances, after long periods of time (i.e., cellulose and hemicellulose).

The anaerobic digesters were originally designed for treating solid waste, such as excess sludge of sewage treatment plants and animal waste. However, these residues are not material with high potential for anaerobic digestion, because the biodegradable material has already lost much of its energy content to the animal that produced it. One way to increase the yield of methane is by mixing or co-digestion of various residues. Therefore, many digesters operate with co-digestion of several kinds of raw materials. For example, in a digester using manure as the main raw material, biogas production can be significantly increased by adding a second feedstock, such as grass and corn (raw materials available on site) or several by-products coming from other locations (slaughterhouse waste, oils and fats from restaurants, organic fraction of household waste, etc.) [194]. The co-digestion of manure with used oil or cheese whey (both in the ratio 75:25 as volatile solids) yielded 361 and 252 Nm³/ton SV, respectively. Yields around 243 Nm³/ton SV were obtained in the digestion of pure manure [193].

Various pretreatment techniques can be utilized to enhance the production of biogas, for instance solid-liquid separation, mechanical grinding (agitator ball mills and homogenizers were found to be best suited, with glass pearls of diameter <1 mm the grinding medium), microbial hydrolysis, addition of alkalis at elevated temperature, silage, acid (HCl, H₂SO₄), alkaline (NaOH, KOH, Ca(OH)₂, alkaline peroxide), oxidative (OH and HO₂ radicals), heat (pressures above 10 bar and temperatures above 150 °C), and ultrasound (frequencies about 40 kHz) [195,196].

Another way to improve the processes of anaerobic biodegradation is through pretreatment of the residue with enzymes: cellulases, cellobiases, endoglucanase, xylanases, pectinases, laccases, manganese and versatile peroxidases, amylases, and proteases. Enzymes enhance the biogas yield and reduce the viscosity of the fermentation media or the feedstock.

A residue which has been extensively investigated with respect to pre-treatment techniques is the biomass of microalgae (third generation biomass). Enzymatic methods involve the use of hydrolytic enzymes, which convert cell wall components (cellulose and hemicellulose) into smaller polymers, which are more easily digested by the anaerobic bacteria. This technique does not present the risk of releasing toxic substances, which is an advantage compared to the chemical pretreatments. Ometto et al. [197] used commercial enzymes (Depol™ 40L—mixture of cellulase and endogalacturonase, Depol™ 220L—alpha amylase, Lipomod™ 957—mixture of esterase and protease, and Lipomod™ 166P—esterase from Biocatalysts Ltd., Cardiff, UK; and Pectinase P2611 from Sigma Co., Ltd., Irvine, UK), used alone or mixed, in the pre-processing of the microalgae *Scenedesmus obliquus*, *Chlorella sorokiniana*, and *Arthrospira maxima*, obtaining very significant increases in methane yield. Enzymatic hydrolysis increased 12 times the methane production, with productivities in the range of 477–730 mL/g VS. Using all enzymes together, further increases were achieved: methane production increased 16-folds employing *A. maxima*, 6.7-folds using *S. obliquus* and 3.5-folds utilizing *C. sorokiniana*. Mahdy et al. [198] studied the improvements of biogas synthesis in semi-continuous anaerobic digestion using *Chlorella vulgaris* after the substrates pretreatment with proteases (Alcalase 2.5 L provided by Novozymes, Denmark). 2.6-fold increased methane yield, 45% COD solubilization and 77% nitrogen mineralization were detected when compared to the CSTR fed with raw biomass. However, the cost of commercial enzymes is still very high, which poses an obstacle to large scale implementation of this treatment.

Deublein and Steinhauser [195] reported that the addition of cellulases and proteases in sewage sludge digesters results in an increase of 20% in the digestion of some reactors. The tests also showed that the addition of the biocatalysts had economically positive effects, such as less use of flocculating agents and reduced costs for disposal of the sludge, with a corresponding enhancement in the velocity of dehydration of sludge and biogas production. Hydrolytic enzymes which are used in enzymatic compounds decompose cellulose, xylan, hemicelluloses, pectins, cuticula, lipids, glycoproteins, and lignin. Such a compound is obtained from enzymes of pure culture as the fungus *Trichoderma reesei* and marketed in a spray-dried or liquid form [195]. The addition of solid enzyme preparations rich in lipases on anaerobic biodegradation of wastewater from the food industry also has beneficial effects, as presented in Section 3.1.

The use of methane contained in biogas as a source of additional energy for the industrial system has attracted great interest. It can be used for steam generation in boilers or converted into electrical energy, which can be exported to the interconnected electric system. Ogejo and Li [199] observed that biogas produced in the co-digestion of dairy and poultry processing industry (0.072 to 0.8 m³/g SV with 56% to 70% methane) was sufficient to maintain a 50 kW generator for up to 9 h. As a mean value, 18.5 to 40 kg of VS used in the anaerobic digestion unit can yield 10 ± 5 m³ of biogas, when 65% removal of SV is reached. This shows a electricity generation of 12.5–33.6 kWh biogas per day, assuming an efficiency of the generator of 35%–50% [105].

Besides the energy produced, other factors like renewable energy credits, carbon credits and green seals for electricity should be considered because they add environmental benefits to the anaerobic digestion process, and subsidies for incentive programs in order to make treatment systems more economically viable.

4.4. Biohydrogen

Concern about energy supply has been boosting the development of alternative fuels. From this point of view, the development of tools for biological hydrogen production from biomass emerges as a promising alternative.

The biological processes for H₂ production have been gaining great importance because of the possibility of using renewable sources or waste materials, thus decreasing the amount of waste stored in industries [200]. In addition, these processes are suitable for decentralized energy production in small-scale units located in places where waste material or biomass are readily obtainable, preventing the additional price of transportation and logistics [201]. Biological procedures are usually performed at atmospheric pressure and ambient temperature. This leads to decreased energy consumption and a favorable energy balance [202]. Among the biological processes for H₂ production, anaerobic fermentation is very interesting, because the increased production of hydrogen as compared to other biological processes and the possibility of utilizing agricultural or industrial waste materials [200,203–205].

Anaerobic fermentation consists in a biological process in which a consortium of different types of microorganisms promotes the conversion of complex organic compounds (proteins, lipids and carbohydrates) into simpler products like alcohols (butanol, ethanol), volatile carboxylic acids (propionic, acetic, butyric or isobutyric acids), CO₂, H₂, and CH₄.

A wide variety of materials rich in lipids, proteins and/or carbohydrates can be utilized as substrates in the production of H₂ by anaerobic fermentation. However, as described in numerous studies, carbohydrates constitute the preferred organic carbon source in the fermentation process [204,206]. Availability, biodegradability and cost are the main criteria for selection of appropriate substrates for the H₂ fermentative production. Simple carbohydrates, like glucose or sucrose, are readily biodegradable. Therefore, they are used as model substrates for hydrogen biological production. However, pure carbohydrates have a too high price for large-scale H₂ production. The utilization of residues as substrates for H₂ production has attracted great interest. The conversion of waste or effluents into H₂ can be considered quite environmentally and economically attractive, due to the generation of renewable energy in association with resource recovery and low-cost waste management [205]. Thus, fermentation of different bacteria utilizing diverse waste materials as substrates has been employed to produce H₂ p. Table 6 presents a comparative analysis of recent studies of H₂ production by anaerobic fermentation from waste materials.

According to Show et al. [207], the main components of feedstock for the future H₂ production will probably be resulting from primary wastes and “green waste” (energy crops). This is because the existence of a high proportion of microbial transformable carbohydrates in green wastes. These authors stated that green waste is a complex polymer composed of lignin, hemicellulose and cellulose. Anaerobic fermentation may transform hemicellulose and cellulose in hydrogen, but lignin is unmodified under anaerobic conditions. In this case, the delignification step of green wastes could be necessary [207,208]. Another chance is the utilization of lignin also for energy production and the carbohydrate fractions for other purposes. This approach opens up the possibility of 2 G ethanol-hydrogen integration, where the use of residual streams of 2 G ethanol production could be exploited for hydrogen and obtaining sequential methane, as explained below.

The use of waste materials for H₂ production has gaining importance to support environmental sustainability. However, most of the organic fraction remains soluble after the fermentation treatment [209]. Sequential production of H₂ and CH₄ utilizing a two-stage process has been considered as an alternative to improve the viability of organic fraction soluble treatment. This system includes the separation of methanogenic and acidogenic processes for the synthesis of H₂ and CH₄, respectively. In the first stage (acidogenic process), organic matter is degraded into organic acids and H₂, and in the second stage (methanogenic process), organic acids are metabolized to CH₄ and CO₂ [210]. The purpose of using a two-stage configuration for the synthesis of H₂ and CH₄ is to optimize each process separately. In addition, previous studies showed that the two-stage strategy for the synthesis of H₂ and CH₄ is more efficient in production of energy than a single stage process for CH₄ production [211,212]. A recent revision showed that the sequential production of H₂ and CH₄ has a higher potential energy than the production of CH₄ in a single stage process.

Table 6. Hydrogen production by anaerobic fermentation from waste materials.

Substrate	Inocula	H ₂ production Generation Performance	Reference
Corn stover	River sediments Anaerobic granular sludge	4.17 mmol H ₂ /g utilized sugar 2.84 mmol H ₂ /g utilized sugar	[213]
Rice mill wastewater	<i>Enterobacter aerogenes</i> and <i>Citrobacter ferundii</i>	1.74 mol H ₂ /mol reducing sugar	[214]
Corn stalk	Cow dung compost	2.56 mol H ₂ /mol hexose	[215]
Rice straw	Pilot-scale anaerobic reactor for H ₂ production from municipal food waste	2.1 mol H ₂ /g COD removal	[216]
Sugarcane vinasse	Seed sludge from distillery plant	2.86 mmol H ₂ /g COD added	[217]
Whey powder solution	Biosolid pellets from the wastewater treatment	0.025 m ³ H ₂ /Kg COD	[218]
Corn stalk	Culture microbial from brewery wastewater treatment	98 mL/g TVS	[219]
Switchgrass	Anaerobic granular culture from a brewery wastewater treatment facility	2.56 mol H ₂ /mol hexose	[220]
Crude glycerol	<i>Klebsiella</i> sp. TR17	44.27 mmol H ₂ /g glycerol consumed	[221]
Wooden chopsticks	Enriched culture from an hot spring	195 mL H ₂ /g total sugars consumed	[222]
Food waste	UASB reactor of the dairy industry	149 mL/g VS added	[223]
Synthetic media for different substrates related to biofuels production (hexoses, pentoses and glycerin)	Municipal sewage treatment plant	4.24 mol H ₂ /mol sucrose; 2.19 mol H ₂ /mol glucose; 2.09 mol H ₂ /mol fructose; 1.88 mol H ₂ /mol xylose and 0.80 mol H ₂ /mol glycerin	[224]
Residual glycerin from biodiesel production	Municipal sewage treatment plant	2.44 mol H ₂ /mol glycerin	[225]

5. Pharmaceutical Products and Chemicals

Biocatalysis may become a green technology to produce chemicals with higher yield and purity.

Enzymes are already utilized in the production of around 2/3 of industrial-scale chiral compounds, because of the higher yields, better crystallization, salt breaking, and easy reuse of the chiral auxiliary [226]. Diverse examples of chiral medicaments are produced by biocatalyzed process, which include atorvastatin (Lipitor), rosuvastatin (Crestor), sitagliptin (Januvia), and montelukast (Singulair). Industrial biocatalysis are still an exception and not a rule, although the use of enzymes has been gaining increasing attention for the organic synthesis of high added-value products, such as pharmaceuticals, flavors and fragrances, vitamins, and fine chemicals as well as for some commodities [156,227]. Companies such as Avecia, Basf, Evonik, DSM, Dow Pharma, and Lonza use enzymes or cells for chiral synthesis of their products [228]. Evonik is also producing specialty esters, aroma compounds, and cosmetic agents using immobilized lipases [229]. According to OCDE, over 300 industrial processes are based on microbial enzymes [230]. In a recent review, Straathof [7] described several possibilities of biomass transformation into commodities through the use of enzymes or cells, in other words, biobased and bioproduction of commodities. Around 15 classes of compounds are mentioned and over 60 products had the synthesis route described and yields evaluated. Considering this data review, there are more than 20 commercial-scale processes for the production of commodities using enzymes or cells with about 10 under pilot production or development, including hydrocarbons, alcohols, carbohydrates, carboxylic acids, esters, amines, and aminoacids [7]. Bozell and Petersen [8] also reported the most promising structures from biorefinery carbohydrates, according to the US Department of Energy by chemical or enzymatic/fermentative approaches. As previously mentioned in this paper, authors have also analyzed the difference between fuels and chemicals technology in order to understand the great challenge to establish a biorefinery. Moreover, it is easier to commercialize a high value product obtained from a bioprocess than commodities. Although the road is long the path is already being paved.

6. Summary and Outlook

The present review covers very important topics of residue and co-product exploitation, not only for waste minimization but also for adding value for different production chains. Biocatalyzed processes have received great attention as a rational and efficient conversion option. However, it is impossible to exhaust all potential applications of biocatalysts and residues to obtain valuable products. In fact, it is precisely this aspect—as well as its corresponding industrial application—that makes this field of study a strategic one.

The traditional concept of production should be redesigned, not only to improve production processes, but mainly and undoubtedly for the need of environmental preservation and improvement of occupational health. The examples dealt with in this review showed the possibility to improve different production sectors: chemicals, fuels, and energy. Some of the examples are still under development, others are only potential opportunities, but the already implemented processes are very successful and stimulating study cases that must be replicated worldwide.

The rational use of resources is an alternative for reducing historical social gaps and the decentralized characteristics of this type of technology could also help diminish social differences.

Acknowledgments: The authors are grateful to FAPERJ, CNPq, PETROBRAS, FINEP, PRH-ANP (all Brazilian), and MINECO (Spain) for financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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