Chapter 5
Biotechnology Application of Pretreated Biomass

Among the proposals for the application of pretreated biomasses, those that make possible the realization of the circular economy appear as alternatives in several areas of biotechnology [1]. Given this circular economy proposal, processes for this purpose can be adapted. When referring to pretreatment methods, some indicators should be considered, including energy cost, formation of inhibitors, sugar content (in some cases as production of ethanol), yield and its effects on the environment, and if necessary, existing methods can be adapted [2, 3].

In the global scenario, the loss of food and consequently the generation of waste is a major challenge. Some 222 million tons of waste are produced by developed countries, because approximately 40% of these losses derive from post-harvest and processing of food [4]. Some residues may be returned to supplement the food chain; however, others will be transformed into a source of biomass for processes with a biotechnological bias. In this development of technology, it is essential that these residues are raw materials with potential for industrial application that may reduce the impacts of inadequate disposal of waste in the environment, and that instead add value [5, 6].

The spectrum of application of these biomass possibilities is broad; focusing on biotechnological processes can subdivide the fate of these raw materials into three major categories: (a) enzyme production, (b) bioenergy, and (c) waste management. Figure 5.1 illustrates some of the application paths for these pretreated biomasses.

5.1 Production of Enzymes from Pretreated Biomasses

Industry is attracted to enzymes as biomolecules with specific actions and biocatalysis potentials in various reactions. The search for increasingly optimized and efficient processes drives the demand for rapid, low cost, and dynamic catalysis reactions; in this regard, enzymes perform admirably [7].

The commercially produced enzyme sector is consolidated worldwide and commands the market with enzymes of industrial interest that act in specific ways in

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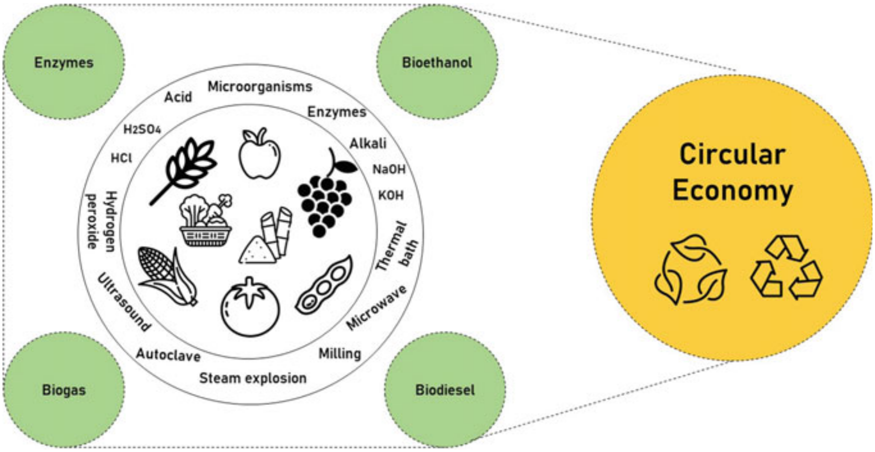

Fig. 5.1 Possibilities of application of the biomasses available in the world matrix, as well as viable pretreatments used for biotechnological processes within the principles of the circular economy. *Source* Authors

various processes. Biomasses are compelling alternatives, performing essential functions. In biotechnological processes, they create the potential to generate lower-cost enzymes. They must possess specificity and capacity to adapt to adverse situations, in addition to stimulating the principles of the circular economy, obtaining new products through residues [8–11].

In the scenario of enzymatic production through residues, microbial strains appear as an essential part of the process, because the production of enzymes by fermentation occurs through the action of microorganisms (mainly fungi and bacteria) in these substrates. As products, there is a range of enzymatic production. Various (pretreated or untreated) residues are sources of enzyme production with high added value that are essential for industrial and technological processes. These include amylase, cellulases, xylanase, and laccase, among others, all of which are produced by microorganisms [5].

Cellulases have the potential to hydrolyze biomasses composed of cellulose. These in turn are popularly known as lignocellulosic biomasses and because of their complex nature. This is because of the simultaneous action of three other enzymes (endoglucanase, cellobiohydrolase, and β-glycosidase) that act on specific parts of the cellulose, breaking long chains in short chains, until obtaining glucose [12].

Xylanases aid in the breakdown of xylan formed by xylose (pentose) and present in biomasses containing hemicellulose. The literature suggests that the microorganisms such as *Trichoderma reesei*, *Humicola isolens,* and *Bacillus* are excellent producers of this enzyme; cellulases and xylanases also form an enzymatic complex, composed of endo-1,4-β-xylanase, β-xylosidase, α-arabinofuranosidases, and esterases. Xylan is considered heterogeneous; therefore, the synergistic action of an enzymatic pool is necessary [12].

Peroxidases are reductive oxidizing enzymes that consist of the enzyme lignin peroxidase and manganese peroxidase. The former acts on biomasses containing phenolic and non-phenolic aromatic compounds and produces cations and the latter acts by oxidizing phenolic substrates [12, 13].

Following the oxidative enzymes, the laccases act by oxidizing biomass that contains copper, in plants, insects, and microorganisms. Laccases are widely used in the degradation of lignin present in the biomass used in bioprocesses. In this sense, white-rot fungus acts through laccase [12].

Keratinases are in the class of proteases that have potential for performance in complex substrates, especially keratinous ones, with heterogeneous structures that are difficult to degrade [14–16].

Lipases act on water-insoluble substrates, catalyzing reactions such as esterification, hydrolysis. They structurally modify oils and fats by specifically catalyzing these substrates. These enzymes are responsible for the breakdown of long lipid chains into smaller chains of fatty acids [17].

Amylases catalyze the breakdown of long starch molecules into smaller chains such as maltose and glucose. These enzymes are of great industrial interest, mainly in the productive sectors of paper, detergents, syrups, and sweeteners. Because of their wide use, they represent a significant portion of the world market for enzymes, about 25% [18–21]. Pectinases are of great importance mainly to the food industry, because they can be used at several stages of fruit processing to facilitate stages of development of the final product, essentially those related to the clarification of juices, wines, coffees, and teas [22, 23].

It is possible to obtain an enzymatic cocktail by means a series of biomass; the formation of enzymes is only possible with the presence of microbial strains capable of using these biomasses as source for their development and enzymatic production. In some cases, the microorganisms are not able to access them, so the pretreatments act as facilitators of these processes [5, 12].

Studies of enzymatic production by means of residual biomass aim not only to obtain new products, but also to evaluate wastes that would be discarded, thereby stimulating the development of the circular economy. In this sense, the possibilities of biomass are amplified. Some of them are summarized below, highlighting enzymes that can be obtained from these sources. The need or lack of need for pretreatment of biomass is displayed in Table 5.1.

5.2 Production of Bioenergies from Pretreated Biomass

The world's energy demand has experienced exponential growth, on account of which high prices of fossil fuels and reduction of natural resources becomes inevitable. Therefore, the development of environmentally sustainable technologies using alternative and low cost of biomass presents greater potential than conventional fossil sources [7].

Table 5.1 Compilation of enzymatic production from the evaluation of residual biomasses in the absence or presence of pretreatment methods

Enzyme	Source of biomass	Pretreatment	Reference
Cellulase	Soybean hulls and waste paper	Autoclave	[24, 25]
	Corn cobs, carrot, orange, potato, pineapple peelings, wheat bran, wheat, straw, sawdust, and rice husk	Alkali	[24, 26]
	Rice husk, soybean hulls, sugarcane bagasse, powder toothpick, and yerba mate	Autoclave	[1]
	Tobacco solid waste	Milling 1% H_2SO_4 NaOH in ratio 1:5 (w v^{-1}).	[27]
Xylanase	White and red grape, vine shoots trimming and grape stalks from the winery industry. Organic crude olive pomace and exhausted olive pomace, and brewer's spent grain	*	[28]
	Grape pomace	Autoclave	[24, 29]
Peroxidase	By-product of olive oil extraction	*	[30]
	Rice bran	Milling Sodium phosphate buffer (pH 5.0) at a ratio of 1:10 (w v^{-1}) under mechanical agitation	[31, 32]
Laccase	Fruit juice waste	*	[33]
	Soybean pod and coffee husk	NaClO 0.5% Dry, crush and sieve	[34]
	Olive leaves	Milling and sieve	[35]
Keratinase	Human hair, pig hair, chicken feather meal, raw chicken feathers, and bovine horn	*	[16, 36–38]
Lipase	Waste cooking oil	Ultrasound	[39]
	Mango residues from juice preparation (peel and seed)	Milling	[40]
Amylase	By-products of wheat	Milling	[20]
	Kitchen waste and peels of vegetables	Alkali (NaOH) and autoclave	[24, 41]
	Banana peel	Wash (H_2O), milling and autoclave	[24, 42]

(continued)

Table 5.1 (continued)

Enzyme	Source of biomass	Pretreatment	Reference
Pectinase	Citrus pulp of floater	*	[43]
	Melon peel	Chemical (citric acid)	[44]
	Potato pulp	Acid (sulfuric, hydrochloric and citric)	[45]

* Not provided

To exploit these biotechnologies in realistic scales, it is necessary to study the stages of the process, especially with regard to the raw material being used. Lignocellulosic biomasses are notable for their potential to produce bioenergies; however, they often require high energy and process costs introduced by pretreatment [7, 46, 47]. Therefore, the search is underway for biomasses that are cheaper, more efficient and that allow promotion of the circular economy. Biomass from the food sector has been presented as an opportunity for innovation, primarily in the sense of having low costs and acting as a substrate for the synthesis of biotechnological products with high added value [7, 48, 49].

Considering the imminent shortage of fossil fuel reserves and the high price of automotive fuels, as well as the large amount of food lost during processing, there is considerable interest in renewable biomass with high energy. Studies regarding the transformation of this biomass as substrate for the application in biorefineries have already been conducted [7, 50]. The concept of biorefineries refers to all biomass (including biofuels) that can be used for the energy sector. The principle of this process is the premise of obtaining technological, economically viable, and environmentally sustainable processes [7, 51].

Second-generation biofuels are those that use residual biomass from other processes, mainly lignocellulosic ones; for this reason, they require additional stages, i.e., pretreatments. The efficiency of pretreatment is related to the potential of simplifying biomass through low-cost techniques, low energy demand, high yields, and the lowest possible impact on the environment [3]. Lignocellulosic biomass is also compelling in the sense of reducing greenhouse gas emissions and non-competition with agricultural crops, consequently directly affecting the food sector, because this occurs when treating biomass as first-generation biofuels [12, 52].

Bensah, Kádár and Mensah [3] used lignocellulosic biomass in your study, rubberwood (*Hevea brasiliensis*), bamboo wood (*Bambusa vulgaris*), Siam weed (*Chromolaena odorata*), and elephant grass (*Pennisetum purpureum*). The biomass underwent a combination of pretreatments: milling in the knife mill (2-mm), alkaline treatment (KOH), and glycerol, after which the samples were autoclaved, followed by enzymatic hydrolysis (cellulase and xylanase). Ethanol fermentation was carried out using *Saccharomyces cerevisiae*. KOH pretreatment was the most promising, producing the highest amount of ethanol (9.8 g 100 $g_{biomass}^{-1}$).

Some studies have also evaluated the potential of eucalyptus biomass for the production of second-generation ethanol. The biomass was pretreated with a combination of the solvent and acid method (50 mM H_2SO_4). As a result, the rate of enzymatic hydrolysis was increased by 94.3% for one kilo of pretreated eucalyptus biomass, suggesting that the method was promising for efficient conversion of cellulose to glucose for subsequent application in the production of bioethanol, as well as for generation of high-value-added products, including xylitol and phenolic lignin resins that are widely used industrially [53].

Agricultural biomass residues are usually harvested from crops and are transported to a central depot to continue to biorefineries, their final destination. Recent studies have sought to simplify the logistics processing of this type of biomass, decentralizing the pretreatment stage, such that the costs of transportation would be significantly reduced [54–59]. The pretreatment, in this case, must be dry, because the biomass needs to be dry for transportation; furthermore, if water is used in the process, it will need to undergo treatment, in the same, way pretreatments that require high energy consumption (such as steam explosion) not are viable [54, 60]. The modified diluted sulfuric acid (dry acid) pretreatment was applied to crop biomass residuals involving corn, wheat, and rice straw; this increased the initial biomass solids content by 70% by reducing residual water. As a final result, 260 kg of ethanol can be produced from one metric ton of pretreated biomass, a relevant yield when compared to the yield of liquid ammonia pretreatment, in which a maximum yield of 205 kg of ethanol from one metric ton of biomass [57, 61, 62].

In spite of the environmental appeal surrounding the use of residual biomasses in high value-added biotechnological processes, care must be taken with respect to the pretreatment used, because it may end up making the whole process unfeasible. Therefore, a comparative approach is needed and aimed at investigating environmental performance of various pretreatments and estimating the consequences of these techniques. What is required is a scenario in which lignocellulosic biomass undergoes various pretreatments, and identifying the technique that presents the lowest environmental impact and greater biomass conversion efficiency for ethanol. Such studies would quantify the entrances and exits of the process, including indicators such as energy consumption and products and emissions generated. In one such study, the pretreatment techniques used were ammonia, sodium hydroxide, sulfuric acid, and methanol; with regard to the emission of greenhouse gases, the pretreatment with sodium hydroxide was the one that expressed the greatest amount of these gases, about 12.03 kg CO_2, followed by sulfuric acid (7.77 kg CO_2) and methanol (0.0019 kg CO_2). A relevant fact in this study is that methanol was also the most effective treatment for the conversion of biomass to ethanol, presenting a smaller carbon footprint, demonstrating the potential to become a product for pretreatment [63].

It is worth highlighting that the environmental impact assessment is specific to each process, biomass and type of pretreatment used. In this sense, the important thing is to verify the possibility of reuse, reduction, and recycling of products or by-products during the pretreatment process with the purpose of minimizing the generation of effluents and the use of drinking water, stimulating environmentally safe processes.

Microalgae are alternative biomasses for the production of biofuels, primarily on account of their formation containing carbohydrates that can be transformed into starch, glucose, polysaccharides, and absence of lignin, facilitating their hydrolysis; however, in the same way as with lignocellulosic biomass, microalgae need to go through pretreatment, which in this case aims to break their cell wall and release compounds of interest for ethanolic fermentation as the starch that is trapped within the cell [64–66]. There are a number of pretreatment methods that can be employed for this purpose, some of which have already been mentioned in Sect. 3 of this volume: acid treatment, ultrasonic, hydrothermal, biological, and enzymatic, among others. Recent studies have used the combined treatment of acid and water at high temperature and pressure (hydrothermal) of the biomass of *Chlorella* spp. to evaluate the production of ethanol. Using experimental and statistical analysis, the authors obtained a maximum yield of 5.1 g L^{-1} of ethanol concentration, with intermediate temperature (130 °C), maximum time (40 min), and maximum concentration of sulfuric acid (1.5 v v^{-1}) among the trials in the studied range. The concentration of the acid was the only variable that had a significant effect on ethanol production from the pretreated microalgae biomass; this can be explained by the tests in which no acid was used and also no ethanol production, possibly due to the low concentration of glucose in the treated biomass; therefore, it is understood that with the presence of the acid, rupture of the cell wall occurred, facilitating the release of sugars [66].

In addition to the production of bioethanol, the lignocellulosic biomass also has potential for generation of bioenergies by means anaerobic biodigestion of these residues, that is, for the production of biogas. Other biomasses including agricultural, landfill, food, and aquatic biomass residues (e.g., microalgae) can be used as substrates for energy production [67].

Raposo et al. [68] compiled information regarding the type of biomass, pretreatment, and biogas yield. The most promising biomass were corn straw and empty fruit bunches, both pretreated in alkaline form, as well as straw from beans, pretreated in an autoclave. They reported yields of 372.4, 404, and 440 mL CH_4 gVS^{-1}_{added}, respectively.

Venturin et al. [69] studied only one biomass, corn stalks, that were subjected to various pretreatments: varying concentrations of sulfuric acid and hydrogen peroxide in an orbital shaker. The authors obtained interesting results. With the alkaline pretreatment (peroxide) there was an increase in biogas production of 22%, in addition to removing 71.6% of the lignin and 19.3% hemicellulose providing a cellulose content of 73.4%.

Using biological pretreatments, it is possible to use the natural microbial functions in favor of the treatment process, which in the case of lignocellulosic biomass is to degrade the lignin or to the microalgae, to break down the components of the cell wall [70]. Most fungal pretreatments refer directly to studies for lignocellulosic biomass, aiming to degrade lignin, for which the fungi of white rot, brown rot (Basidiomycetes family), and rotting fungi (Ascomycetes group) are considered ideal for these processes. A disadvantage of this pretreatment is the possibility of removal of components important for the later stages, e.g., significant losses of cellulose and hemicellulose caused by use of non-selective fungal strains. Some studies have identified potential fungal strains pretreatments considering the high efficiency of lignin removal and the low losses of cellulose and hemicellulose during treatment. The fungus *Ceriporiopsis subvermispora* stands out in this scenario because of its potential to remove lignin with very low loss of cellulose. In these studies, the biomasses pretreated by the fungus were corn straw, rubber, grasses, and hardwoods [71–73], obtaining high overall process efficiencies. This was due to the selectivity of the fungi that secrete lignolytic enzymes and assist in the hydrolysis of the biomass.

In a study aimed at biogas production, a pool of lignocellulosic biomass, corn straw, wheat straw, flax, hemp, miscanthus, and willow were used. All underwent enzymatic treatment with laccase and peroxidase enzymes, both produced by microorganisms (*Trametes versicolor* and *Bjerkandera adusta*, respectively). Biogas production through the addition of a bovine manure effluent in these pretreated biomasses has enhanced the yield and quality of biogas and treated effluent [74].

Observing the yield of the fermentation process after the pretreatment step gives us the information on how effective the chosen method was. The literature suggests higher yields in microalgae biomass, because their structure to be obtained by the pretreatment is more flexible; by contrast, the lignocellulosic biomasses present lower yields and this is due to their structure being more rigid and more difficult to access by enzymes (cellulases, xylanases, among others) or hydrolytic microorganisms. This can be seen in studies in which raw biomass yields were quantified untreated in their crude form. The differences between the two types of raw materials are presented in Table 5.2.

It is difficult to reach objective conclusions about these processes. It is necessary to have a broad view of the whole structure and composition of biomass, conditions of pretreatment processes, yields, as well as technological and economic viabilities, among others. One can see the vast possibility of applying pretreated biomass to stimulate a world energy sector that is facing a serious crisis. These approaches allow the insertion of frequently unused biomasses into biotechnological processes with high benefit.

5.3 Valuation of Residues from Pretreated Biomass

Usually, waste management is carried out in the most well-known ways, composting, incineration, or disposed in landfills. Nevertheless, this does not mean that these are the most appropriate practices, despite worldwide acceptance [7, 78].

The valuation of residues appears as a management possibility, mediated by sustainable conversion of these residues. This approach offers a number of advantages, especially in the economic and environmental sector, as it reduces waste disposal in landfills and consequently decreases the possibility of contamination, stimulating a circular economy culture [7].

Table 5.2 Studies showing the yield differences between lignocellulosic and microalgae biomass

	Biomass	Pretreatment	Yield and application	Reference
Lignocellulosic	Rice straw	Fungal (*Pleurotus ostreatus* and *Trichoderma reesei*)	Yield 120% for methane yield	[75]
	Corn straw	Fungal (*Phanerochaete chrysosporium*)	Yield 263% for ethanol	[73]
	Switchgrass	Fungal (*Pycnoporus* sp.)	Yield 50% for sugar	[71]
Microalgae	*Scenedesmus obliquus*	Enzyme (cellulase, esterase, protease, and endogalac-touronase)	Yield 485% for methane	[76]
	Scenedesmus obliquus	Enzyme (esterase and protease)	Yield 273% for methane	[76]
	Nannochloropsis gaditana	Bacteria (*Raoultella ornithinolytica*)	Yield 114–159% for methane	[77]

Management of the vast accumulation of waste requires efficient strategies. In this sense, it is desirable to focus on the conversion of waste biomass for use in processes of biotechnological interest such as the bioenergy sector [7]. By 2050, it is estimated that the increase in population will lead to an increase in global food production, a determining factor for the implementation of the circular economy. For these reasons, transforming residues into substrates that do not need to be burned or grounded and which have priority to close the cycle are extremely relevant [28].

Among the possibilities of waste valuation, the production of enzymes from residual biomasses appear as compelling low-cost alternatives, but with high added value, because these enzymes often have potential application in biotechnological processes. In this sense, Leite et al. [28] evaluated the production of the enzymes β-glycosidase, cellulase, and xylanase by combining the biomasses of olive mill, winery, and brewery wastes using solid-state fermentation with filamentous fungi (*Aspergillus ibericus*, *Rhizopus oryzae,* and *Aspergillus niger*). They found high activities of cellulase, xylanase, and β-glycosidase, respectively, in the fermentation products. In addition, the enzymes produced oxidative phenolic compounds. Biological pretreatment and production of an enzymatic pool permitted generation of antioxidant by-products in a low cost and environmentally viable biotechnological process.

Another example of biomass valuation is the use of chicken feathers from the poultry industry. A study carried out in Malaysia in 2016 found that about 43 thousand tons of waste feathers were generated during the processing of cut poultry. This waste has a most common destination landfills and incinerators, contributing to greenhouse gases and environmental contamination [79]. Studies have focused on alternative solutions for the management of residue, highlighting the valuation of this residue as a form of biomass for use in biotechnological processes. However, feathers have rigid structures, and keratin must be pretreated so that it can be used in other processes, as described by Cheong et al. [79]. The authors combined pretreatments (alkaline NaOH, microwave, autoclave, and enzymatic with commercial protease) for feather solubilization and protein recovery. They found that degradation of the feathers was low, possibly because of disulfide bonds between the keratin chains that hampered the access of enzymes [80]; by contrast, the tests with pretreated NaOH and microwave presented more efficient results of protein recovery; these techniques may be promising for the utilization of chicken feathers from the protein processing industries.

Animal protein processing demonstrates that keratin-rich residues constitute biomass of great interest for the development of new processes and product valorizations, particularly chicken feathers and swine hairs. Recycling these wastes expands the range of biotechnological applications (production of enzymes, biomolecules, fertilizers, biogas, among others), considering the principles of the circular economy, as well as the environmental and economic sectors involved in these processes [16, 81–84].

India invests heavily in waste management, as a populous country with relatively small territory. Studies of urban waste valuation in these regions are relevant and are technology drivers. Recently, food waste, fruit peel, vegetable peels, and garden pruning have been used as raw materials for biogas production. The total substrate composition was 50% cooked food waste, 25% vegetable peel and fruit peel, and 25% garden waste. A combination of milling and hydrothermal pretreatments was applied at temperatures of 80, 100, 120, 140, and 160 °C with durations of 0, 15, 30, 60, and 120 min. After pretreatment, authors observed better dissolution of carbohydrates, proteins, and lipids. At lower temperatures (80 and 100 °C), the biomass pH also decreased, suggesting thermal hydrolysis; nevertheless, these temperatures were not sufficient to degrade cellulose or hemicellulose. This was made possible under the most severe pretreatment conditions, in which methane production was also increased, reaching a yield of 200 mL g_{VS}^{-1} [85]. This suggests that hydrothermal pretreatment allowed the solubilization of complex organic matter, making the degradation of microorganisms and enzymes present in the biodigestion process more accessible, thereby reducing retention time, and making the process more efficient.

Residual biomass is placed in the waste valuation scenario as an important source in the most diverse biotechnological processes, with the potential to produce high value-added by-products. Although the waste valuation process offers an opportunity and is compelling from an environmental and economic point of view, it presents limitations regarding an efficient conversion. This is basically due to the heterogeneous constitution of these biomasses. In this scenario, studies appear as alternatives to find suitable strategies in which it would be possible to carry out the waste management while extracting value from them [24].

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