Chapter 3
Waste Biomass Pretreatment Methods

Pretreatment of residual biomass is one of the key elements in integrated conversion processes such as biorefineries. Biotechnology projects rely heavily on the efficient, technical, economic, and environmental feasibility of pretreatments. Pretreatment is a unitary operation that precedes a certain process, and it is not itself the ultimate goal of the activity. Nevertheless, the inclusion of this step increases the efficiency of subsequent processes by increasing accessibility to the primordial biomass structure, facilitating access to enzymes and reagents used in the development of high added-value products.

The need for cost-effective pretreatment technologies is the highlight of newly developed biotechnological processes, always seeking treatments that are efficient, with a high degree of activation of key biomass components, the formation of low by-product concentrations and low reagent consumption [1]. Among the pretreatment methods reported in recent literature are physical pretreatments (mechanical, ultrasound, microwave, thermal), chemical methods (alkaline, acidic, oxidative), biological methods (microorganisms and enzymes), and combined processes that include two or more pretreatment methods. The mechanisms of action of each method will be detailed and discussed throughout this section.

3.1 Physical

Physical pretreatment comprises unitary operations designed to modify physical properties of waste biomass without the addition of chemical reagents or microorganisms. Physical pretreatment techniques include mechanics (grinding, screening, extruding), ultrasound, microwave, and heat.

3.1.1   Mechanics

Mechanical pretreatments are widely used to reduce particle size and to increase porosity and biomass surface area. Grinding and screening are highlighted in the literature for waste biomass for simplicity and ease of use. The absence of chemical reagents, as well as the non-generation of inhibitors and toxic products, makes the mechanical processes attractive, especially when subsequent biological processes such as bioenergy production or enzyme production are applied. Mechanical methods are among the most suitable for preliminary treatment of biomass in industrial expansion, resulting in reduced structure stiffness and crystallinity and increasing the concentration of available nutrients in biomass cells facilitating the subsequent processes [2].

Grinding is often used as a preliminary mechanical treatment in combination with other processes such as heat, ultrasound, chemical treatments, acting on biomass through physical force, increasing the diffusion of biomass compounds by increasing surface area and sample uniformity, thereby enhancing system performance [3, 4]. For high lignin structures such as corn husk, when fragmented by particle grinding of 40–60 mm, the cell wall is destroyed, causing disruption in cell structure such that cellulose layers become more available, resulting in particles with high reactivity due to the increase in accessible surface area and due to structural disorder [5].

All processes that occur with biomass are heterogeneous and the reaction rate and yield to obtain the final product strongly depend on the surface area available for the reaction. This is the case of lignocellulosic biomass which when applied in substance extraction processes limits the process of direct diffusion through the complex lignocellulosic matrix. As such, large-scale processing usually includes first-stage milling [1].

The most widespread equipment in the milling process is knives and hammers that differ depending on the size of the milling bodies; however, there remain others such as disk mills, ball mills, bead mills, and vibration mills.

In the hammer mill, the grinding process is performed in two steps. The first occurs by the impact of biomass with the grinding bodies, and in the second, the rotor presses the particles against the screen mesh of the equipment, where the material is crushed. This equipment is widely used and has high productivity and relatively low power consumption. The main limiting factor is that reducing the size of the screen mesh reduces the performance of the equipment, creating the difficulty of developing a mesh capable of supporting the mechanical load during grinding. Nevertheless, this is the most commonly used equipment for preliminary biomass treatment, reducing particle sizes from tens of centimeters to tens of millimeters [1].

Destruction models and force theories for biomass grinding processes are myriad. In the application of these devices, the mechanism that explains particle reduction is based on the type of mechanical action, and the same equipment involves several mechanisms. The main types of action in grinding processes are cleaving, shearing, crushing, cracking, cutting, sawing, abrasion, limited impact, and free impact [1, 6]. For the process of cleavage, shearing, cracking, and sawing, it is necessary that the

biomass particles have sizes comparable to the equipment working body. With units above millimeters, these are generally used for primary biomass preparation. The crushing action is suitable for fragile biomass. Cutting and sawing reduce particle size by several centimeters and are usually applied in robust biomass grinding equipment. Finally, actions such as cutting, abrasion, and impact are used to grind rigid biomass such as plants [1].

Pretreatment using a knife mill has been described by Lee and Mani [7] as fiber shear action for nanofibril cellulose production, with relatively lower specific energy expenditure than other equipment used for this same process. Pirich et al. [8] compared various mechanical pretreatment processes, including the colloid milling process, characterized by grinding action, and shown to be essential in the isolation of cellulose nanofibrils. In this context, it is important to highlight that the economic costs involved in the grinding processes do not make the process unfeasible and must be evaluated for each reality and biomass varying for each production; therefore, the optimization of processes and characteristics of biomass determine much of the consumption of this stage.

Another mechanical process is extrusion, used for fractionation of residual biomass. This is a simple process, with mild temperature conditions, not necessarily needing the addition of chemicals, and operating continuously. This process is effective and versatile, effectively mixing pretreated biomass. The yield is continuous, and there is the possibility of adaptation to various process configurations [9, 10].

In the extrusion process, the biomass passes through an extrusion barrel, where it is subjected to high shear. As a result, regions of high pressures and temperatures develop that cause the defibrillation and shortening of the fibers that compose the biomass [10–12]. During the process, the moisture of the biomass comes out of steam as a result of the sudden drop in pressure, causing pore expansion and opening [12, 13]. The high mechanical shear developed inside the extruder barrel breaks down the biomass structure, and this process facilitates contact between residual biomass structures and subsequent processing agents [11, 12].

Extrusion stands out among the mechanical methods because it is a viable technology, without generation of by-products, acting under mild conditions, reducing the degradation of compounds, and capable of fractionation with high solids loads. It works with considerably larger biomass sizes than other methods, leading to greater economic profitability than processes aimed at reducing biomass size [10, 12].

Compared to residual wheat and soybean meal biomasses, mechanical milling processes using hammer mills and extrusion have shown to be promising. The extrusion process showed higher yields compared to residual wheat bran biomass. Higher temperatures for shorter times and lower temperatures for longer times gave rise to extrusion process with higher yields [11].

3.1.2   Ultrasound

Ultrasonic energy accomplishes pretreatment process by cavitation, the result of the propagation of strong waves of frequencies higher than 20 kHz that propagate longitudinally in liquid with alternating pressure periodically in a continuous cycle of rarefaction and compression; this generates negative and positive pressures, respectively [14–16]. As acoustic energy propagates in the liquid and generates negative pressures in the medium, gaseous microbubbles form and fill with vapor; dissolved gases distribute throughout the liquid [15, 17]. The negative pressure that results in microbubble formation is called the cavitation threshold [15]. Microbubbles expand and retract, reaching a maximum diameter of 4–300 mm, varying according to the frequency of the ultrasonic wave pulse. This phenomenon is called stable cavitation when microbubbles are generated under conditions where the maximum sound pressure. In the rarefaction cycle, it is not strong enough to force the bubble to expand its collapse radius [15, 16, 18]. The compression and rarefaction (radial oscillation) cycles due to the pressure oscillation in the medium caused by the ultrasonic waves cause the microbubbles to continue to grow over a few cycles until they reach a critical diameter, high temperature (5000 K), and high pressure (100 mPa), enter an unstable stage, and collapse violently, generating a microjet with dominant shear stress, turbulence, increased pressure and temperature at the site. This process is referred to as "transient cavitation" and is referred to when acoustic pressure exerted on the microbubble causes it to expand at its resonant radius amid several acoustic cycles, resulting in collapse. This force is sufficiently strong to destabilize structures, disrupt cells, and increase mass transfer [15, 16, 19–21]. Collapse occurs within approximately 400 µs [16, 22].

Cavitation occurs in a liquid system, and when applied to solid biomass emerging from the liquid, the cavitation bubbles collapse and generate high-velocity microjets toward the biomass surface, causing flaking, erosion, breakdown of cell walls, so as to increase the diffusion of biomass matrix compounds, inducing intense macroturbulence, micromixing, and consequent collision [15, 23]. These phenomena increase particle reactivity. Mass transfer is also increased because of increased surface area [23].

Ultrasound describes the result of the transformation of electrical energy into thermal and vibrational energy that is then converted into cavitation and is also lost by sound reflection. It is through the combination of pressure, temperature, and turbulence that we obtain a variety of effects in ultrasonic systems in the most diverse biomass and end products.

The efficiency of ultrasound in residual biomass pretreatment techniques depends on several factors. Solvent viscosity is a parameter that should be considered when using ultrasound in pretreatment processes, because cavitation requires negative pressure that must overcome the natural cohesion forces of the liquid. Cavitation is diminished in viscous liquids, where the natural cohesive forces are stronger than the negative pressure of cavitation formation. This factor may reduce the process yield. To increase the cavitation threshold, simply increase the viscosity of the liquid

[14, 24–26]. Increasing polysaccharides in the solvent may reduce the cavitation process by increasing the viscosity of the medium [25]. The increase of the solid/liquid ratio in a system pretreated with ultrasound can be achieved to a point where the increased solids in the medium correlate with decreased system yield because of the increase of viscosity, resulting in difficulty of cavitation formation [24].

Another factor that affects the process and should be noted with caution is the temperature of the solvent, which changes viscosity and surface tension, inducing an increase in vapor pressure. As a result, the rate of chemical reactions changes, affecting the threshold and intensity of cavitation and resulting in a greater number of bubbles that will collapse less violently and reduce the effects of cavitation processes [14, 23]. High temperatures near the boiling point of the solvent used in the process may negatively affect ultrasound pretreatment [23]. Optimization of the process temperature is important, considering that, for residual biomass, ultrasonic pretreatment can be conducted at relatively high temperatures giving higher yields. Yield decreases would occur only in regions near the boiling point of the solvent.

Two devices apply conventional high-power ultrasound pretreatment techniques: ultrasonic baths and probes. These systems use a transducer as a power source. The ultrasonic bath is widely used for its simplicity, low cost, and ability to treat several samples simultaneously. This equipment usually operates at 40 kHz and has temperature control. The amount of energy dissipated in the ultrasonic bath is not easily quantifiable and depends on the size of the equipment, the vessel in which the reaction occurs, and the position of the sample within the tank. These factors influence the reproducibility and potency of ultrasonic waves in pretreatment samples [23].

The ultrasonic probe is more powerful than the bath because of the intensity provided by the system that is delivered only by the probe tip that releases energy directly into the solvent where the biomass is emerging, resulting in less energy loss from the cavitation waves. The selection of the ultrasonic probe model should be made by studying the application, biomass, and volume desired [23].

3.1.3 Microwave

Microwave irradiation is a widely used process for biomass pretreatment. Electromagnetic irradiation of microwave equipment operates in the range 0.3–300 GHz, within the electromagnetic spectrum between infrared and radio frequency [27, 28].

Microwaves work via two mechanisms: thermal and non-thermal. Thermal effects are governed by temperature differences, and non-thermal effects (acceleration, change in reactivity and selectivity of biomass) refer to the circumstances of a synthesis that are microwave conditions [28]. There are arguments against the non-thermal effects, particularly that microwave photon energy (0.0016 eV) is not sufficient to break chemical bonds [29].

The electrical component of the electromagnetic field is responsible for heating (thermal effect) during the microwave process through three primary mechanisms:

dipolar polarization, ion conduction, and interfacial polarization. Generally, these mechanisms occur simultaneously [28–30].

The dipolar polarization mechanism is the primary principle of microwave heating that involves the process of dielectric loss heating [30]. When biomass is exposed to microwave frequency, a dipole sensitive to external electric fields tries to align with the applied electric field. When this applied field oscillates, an attempt is made to realign the dipole field to the alternating electric field, though in the presence of a field. High-frequency electrical power does not have enough time to respond to the oscillating field, causing a phase delay that results in fields colliding with one another. In this process, the energy is dissipated as heat by molecular friction and dielectric loss [29, 30]. The amount of heat generated during this process is directly related to the ability to align between the matrix and frequency of the applied field. That is, there is a quick orientation with the applied field, and if the dipole has sufficient time to realign itself, warming will occur [29].

The interfacial polarization mechanism, also called Maxwell–Wagner Polarization, should be considered when applying the microwave process to non-homogeneous biomasses such as biological materials in suspensions or colloids. This process consists of components with varying conductivities and dielectric constants. In the interface area of these components, polarization induces the formation of a charge accumulation region that causes field distortions and dielectric loss, resulting in heating [28].

The conduction mechanism is the heating principle that involves the creation of an induced electric current resulting from the movement of mobile charge carriers (electrons, ions, etc.) under the influence of a microwave electric field. These induced currents are responsible for heating as a result of electrical resistance caused by collisions between charged molecules [30]. The effect of conductivity has a greater influence on system warming than does the dipolar rotation mechanism [28].

Microwave heating differs from conventional heating in that, by means of ion conduction and dipolar polarization mechanisms, the heat wave is generated from within the biomass structure evenly and rapidly [31]. The use of microwaves as a pretreatment technique is based on the heating of biomass by "microwave dielectric heating," which depends on the ability of materials to absorb microwave energy and convert it into heat. The heating characteristics of the biomass subjected to microwave pretreatment depend on the dielectric properties of the material [27–29]. The dielectric properties of a material are a function of the dielectric constant and the dielectric loss factor. The first relates to the ability of the material to be polarized by an electric field and represents the amount of energy that is stored in the material; the second suggests the efficiency with which electromagnetic energy is converted to heat [28].

The use of microwaves as lignocellulosic pretreatment has been performed over the last 30 years. In some cases, transitions from laboratory to pilot scale have already been seen [31]. Compared to conventional heating, this technology has low sugar degradation and by-product formation [32].

3.1.4 Hydrothermal

Thermal pretreatment processes are techniques based on the use of thermal energy to cause agitation and molecular changes in the structure of biomass that may cause defibrillation, chemical bond cleavage, increased surface area, and reduced recalcitrance.

Of all biomass pretreatment technologies, steam explosion has been considered as a potential process for numerous products, primarily because of the low or nonexistent chemical consumption, low monosaccharide degradation under mild process, and neutral conditions. The pH that prevents equipment corrosion as well as the energy consumption is relatively low compared to those of other physical pretreatment processes. Nevertheless, steam explosion has disadvantages such as inhibitor generation and weight loss of the initial dry mass of biomass [33].

Steam explosion operates at temperatures of 140–240 °C and high-pressure conditions at incubation times of seconds to 20 min. The mechanism of action is the result of the mechanical effect of an adiabatic expansion of water absorbed by biomass and the chemical effect of the action of organic acids released during the process, occurring at the first moment of the solubilization of hemicellulose at high temperatures and pressures [34, 35]. The mechanical effect results from the rapid decompression of the equipment where the process occurs, resulting in the internal explosion of biomass fibrils disrupting the structure of the lignocellulosic complex and causing structural changes, particle size reduction, and biomass pore enlargement [33, 35–37]. The pressure and temperature conditions cleave the hemicellulose and lignin bonds, and the secondary explosion caused by the sudden reduction in temperature and pressure disrupts the biomass structure, increasing the solid surface area and causing a disturbance in the crystalline region of the structure [35]. At the end of the steam explosion process, a solid fraction containing partially modified cellulose and lignin is obtained, with a low pH liquid fraction containing oligomers, monomers, organic acids, and phenolic compounds [34].

Another promising technique for thermal pretreatment is liquid hot water (LHW), based on the application of high pressures to maintain liquid water and temperatures from 160 to 240 °C. This is a process with high removal capacity of the hemicellulose fraction as well as changes in lignin structure of the lignocellulosic complex without the addition of chemical reagents, making cellulose more accessible for hydrolysis processes [34, 38]. It has been suggested that, when temperature and pressure increase in the water, there is penetration in pores of the biomass, causing destructuring that leads to acidification of the environment. The latter is caused by the release of organic acids present in the structure, especially acetic acid that acts on hydrolysis of the structure during the process, releasing mainly oligosaccharides in the liquid fraction [34, 39, 40]. The main difference between the LHW and the steam blast technique is that the former does not use rapid decompression for structure defibrillation.

Steam heat pretreatment is a technique with similar mechanisms to the previous ones; the primary difference is the arrangement of the biomass in the reactor, because the material remains at the top, having no direct contact with the water in the liquid

state. This crucial difference causes steam pretreatment to allow higher solids charges than steam blast and LHW techniques. The hemicellulosic fraction is the main target of this type of pretreatment and is removed by contact with steam at high pressure and temperature [34, 41].

Process parameters are crucial for the results obtained in the thermal pretreatment technique, with temperature, pressure, and incubation time being the main factors to be studied. These techniques are considered green and cost-effective because of the process yield and not the chemical application.

3.2   Chemicals

Chemical pretreatment is operations designed to modify physical and chemical properties of residual biomass in the presence of a chemical catalyst aiming for conformational changes in the biomass structure such as cleavage of bonds and generation of specific products. The techniques of chemical pretreatment include alkalis, acids, organosolv, ionic liquids, and oxidative processes.

3.2.1   Alkaline

Alkaline media are popularly used for pretreatment of biomass because they are relatively less expensive than other reagents and have less compound degradation. Among the most widely used bases are sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), potassium hydroxide (KOH), and ammonium hydroxide (NH_4OH).

The efficiency of alkaline pretreatments is associated with the ability of the base to perform biomass delignification and reduction of cellulose crystallinity. It is generally associated with the pretreatment of lignocellulosic biomass for bioenergy production. In addition to acting efficiently in delignification, alkaline pretreatment has advantages such as lower sugar degradation, especially compared to other chemical treatments such as acids or oxidizing agents, and can be conducted at low temperatures and pressures. Nevertheless, depending on the complexity of biomass, longer periods may be required for higher yields [42, 43].

Table 3.1 displays the bases applied in pretreatment processes, aiming to demonstrate recent applications in biomass for various biotechnological purposes. All alkaline pretreatment techniques in lignocellulosic biomass have the common effect of increasing biomass digestibility by altering the lignocellulosic complex.

The action of alkaline pretreatments remains much discussed in recent works. It is believed that the mechanism of alkaline pretreatments in lignocellulosic biomass is based on two principles: the swelling of the biomass structural complex and the reduction of crystallinity, resulting in partial cleavage of lignin structure and solubilization of hemicellulose acetyl groups [50, 51]. Removal of hemicellulose is relevant

Table 3.1 Pretreatment processes applied in biomasses for biotechnological purposes

Reaction	Reaction conditions	Biomass	Main effect	Reference
Sodium hydroxide	2–8% (m m^{-1}) NaOH 35, 55, and 121 °C 24–24 h; 1 h	*Pennisetum hybrid*	– Reduction of hemicellulose and lignin content and increase of cellulose content – Increased surface porosity – Breakage of intra- and intermolecular hydrogen bonds and methyl/methylene of cellulose	[44]
Sodium hydroxide	0.5, 1.0 and 2.0% p v^{-1} NaOH 121, 50 and 21 °C 0.25–1, 1–48 e 1–96 h	Switchgrass	– Reduction in lignin was closely related to temperature: 85.8%—121 °C, 77.8%—50 °C, 62.9%—21 °C, at higher NaOH concentrations and longer times	[45]
Calcium hydroxide	0.02–0.12 g g^{-1} Ca(OH)$_2$ 25–55 °C 7–28 days	*Spartina alterniflora*	– The pH has been neutralized in some samples by acids formed in the process due to the breakdown of ester bonds and neutralizing structural carboxylic acids formed by deacetylation of hemicellulose – Selective removal of hemicellulose and lignin, with cellulose recovery yield between 91 and 98.7%	[46]
Ammonium hydroxide	0.5–50% mass NH$_3$ 30 °C 4–12 weeks	Corn straw	– Preservation of carbohydrates – 55% delignification with the highest NH$_3$ load – Increased digestibility of biomass in the enzymatic process	[47]
Potassium hydroxide	0.5–12.5 g KOH 20 °C 24 h	Wheat straw	– Lignin and hemicellulose content decreased with increasing KOH load – Sugar concentration after enzymatic hydrolysis of pretreated biomass	[48]

Table 3.1 (continued)

Reaction	Reaction conditions	Biomass	Main effect	Reference
Sodium hydroxide	0.07 g NaOH/g of biomass 140 °C 30 min	Corn straw	– High efficiency in lignin removal from biomass – Low structural alteration of lignin in lower-molecular-weight compounds – High concentration of lignin in the pretreatment liquid fraction	[49]

to the effect of pretreatment on cellulose structure. Hemicellulose losses occur for degradation products that may have an inhibitory effect on the subsequent process [50].

Cellulose structure is disturbed by the action of alkaline pretreatment because of the action of solvation process forces, which, in the presence of swelling of the lignocellulosic structure and increase of the internal surface area, causes intermolecular forces of the cellulose to be smaller than forces due to solvation, disrupting the hydrogen bonds of adjacent chains of the cellulosic structure [43]. This process may favor the penetration and propagation of reagents and enzymes in subsequent processes. It is common for the cellulose crystallinity index to increase [42, 44] as a result of the removal of amorphous cellulose that is more susceptible to alkaline hydrolysis.

The intermolecular saponification process is a possible action of alkaline pretreatment, and this is the process that results in the removal of lignin. The increase in the internal biomass surface allows the alkaline agent to access the xylan-linked ester bonds present in hemicellulose with other components. These breakdowns produce charged carboxyl groups that cleave bonds with lignin and other lignocellulosic complex compounds. It is these structural cleavages that allow the breakdown of cellulose adjacent hydrogen bonds reported in the solvation process [42, 43, 50].

In particular, calcium hydroxide promotes lignin reduction through the formation of a calcium–lignin complex, where calcium ions (two positive charges) tend to attract negative lignin charges under alkaline conditions because of ionization of functional groups, and this mechanism avoids intensive lignin solubilization [45, 52]. However, increased calcium loading may reduce lignin dissolution and may attenuate carbohydrate loss, possibly due to the binding of calcium ions with these compounds under alkaline conditions. [45].

Sodium hydroxide is the most often used catalyst, with high delignification efficiency, increased biomass digestibility, relatively fast reaction rate, less formation of biological process inhibitors, and increased surface area of biomass [53]. Nevertheless, between sodium hydroxide and calcium hydroxide, the latter is preferable; because of its safety profile, relatively lower cost, ease of recovery, compatibility with oxidizing agents, and selectivity for the structure of lignocellulosic biomass [46, 51,

54], the residence time of calcium hydroxide pretreatment needs to be longer, as noted in the studies reported in the table below. This factor has to do with the low solubility of the reagent that requires longer residence time to achieve the same yield as the other alkali reagents discussed in this section.

Ammonia-based pretreatments have been highlighted for easy reagent recovery, non-corrosive and non-toxic nature, economically viability, and wide use in fertilizers. In addition, their use and industrial recovery are well-established procedures, with viable processing options for recovery. The effects of ammonia on biomass include delignification, increased surface area, and structural modification of cellulose and hemicellulose [55, 56].

Alkaline pretreatments are interesting for high lignin and hemicellulose residual biomass, as well as in processes where the preservation of carbohydrate structure is desired. These methods are easy to apply, with low generation of inhibitors, and can be applied to various biotechnological processes.

Recent studies have evaluated the use of alkaline pretreatment (NaOH) in maize straw for chemical production. The authors used SEM and found that cell walls of the structure were swollen and that the rupture caused by the pretreatment of biomass exposed the internal areas of the structure, triggering an increase in the porosity of the material. The authors were able to remove between 63.90 and 81.91% of lignin at temperatures at 60 °C, with 1-h pretreatment, and low NaOH concentrations (0.25–0.75 mol dm^{-3}, respectively) [57].

Hashemi et al. [58] studied the effects of ethanolic ammonia pretreatment on sugarcane bagasse for biogas production. The authors observed that lignin–carbohydrate and lignin bonds were hydrolyzed and lignin was removed from the biomass. They also found that glucan and xylan recovery were higher with pretreatment supplemented with ethanol than with ammonia alone. The effect of ethanol on this system is believed to cause soluble xylan to precipitate into solid structures that facilitates the recovery of this sugar for anaerobic digestion processes [58, 59]. Another similar work defined pretreatment for ethanol and aqueous ammonia immersion, now focusing on corn straw biomass, and found that the effect of ethanol contributed to the preservation of cellulose in solid form. The addition of ethanol at 20% (by weight) resulted in an optimal concentration for glucan and xylan digestibility [59].

Alkaline pretreatment (NaOH) in wheat straw reduced the lignin fraction by 36% and significantly reached hemicellulose (35% reduction) after pretreatment [60]. The predicted effects for the reduction of lignin and hemicellulose were associated with saponification and cross-linking cleavage processes between xylan and lignin that also caused increases in internal surface area, as previously reported [61, 62].

3.2.2 Acids

Pretreatment techniques that use acids as catalysts are commonly used for various biomasses at high or diluted concentrations, with inorganic acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and phosphoric acid (H_2PO_4) being most common.

Pretreatment with an inorganic acid in lignocellulosic biomass is widespread on the industrial scale, because it is a chemical reaction facilitated in complex structures and because the process is efficient in fractionating the hemicellulose of the biomass structure by increasing the surface area and accessibility of the biomass structure in downstream processes [32, 63]. Furthermore, this pretreatment may be useful in dissolving lignin in lignocellulosic biomass, even though it generally acts less efficiently with respect to removal of this compound compared to hemicellulose cleavage [64]. Nevertheless, biological process inhibitors such as alcoholic fermentation for ethanol production form during hemicellulose and lignin cleavage, solubilization, and degradation, including furans because of dehydration of monomers and phenolic compounds [65].

When the technique is performed by applying concentrated acid, the temperature is generally low and results in high yield of monosaccharides in lignocellulosic structures derived from the cellulose structure. However, the hydrolysis rate of amorphous cellulose is slow compared to that of hemicellulose that has an amorphous structure; therefore, the concentrated acid technique generates high concentrations of furan inhibitors due to dehydration of monomers of the chemical structure of hemicellulose. Another disadvantage is equipment corrosion, high chemical consumption, high toxicity for the environment, and high energy demand for acid recovery [43].

Another application of the chemical pretreatment is the hydrolysis using dilute acid, where high-temperature and high-pressure applications are required to increase the yield from crystalline cellulose, consuming fewer chemicals than the prior technique. However, this usually results in the degradation of sugars because of more severe temperature and pressure conditions, causing solubilization of hemicellulose chains and dehydration of pentoses and hexoses in inhibitors [43, 66–68].

With the search of continuous advances in biomass pretreatment processes, organic acids have become alternatives to inorganic acids for some biotechnological processes, including dicarboxylic (malic, oxalic, fumaric) and monocarboxylic acids (acetic acid). Compared to inorganic acids, organics have advantages such as lower equipment corrosive capacity and less environmental damage, lower energy demand for compost recovery, longer long-chain cellulose insulation capacity, lower inhibitor generation, and higher pH in relation to inorganic acids [43, 69, 70]. Organic acids are an efficient alternative to the pretreatment of high cellulose and hemicellulose biomasses such as aquatic plants and rice straw [71, 72].

The interaction mechanisms between biomass and acid in pretreatment processes strongly depend on the factors involved in the process, especially the temperature and composition of the material subjected to pretreatment. The main purpose of acid application in biomass pretreatment reactions is to weaken or disrupt the chemical structure, being generally based on hemicellulose hydrolysis and reduction of crystallinity of other compounds [73, 74]. It is suggested that this action occurs through the cleavage of aryl ether bonds, a set of abundant bonds in lignin macromolecules that

have low binding energy that facilitates direct cleavage in this branch. Through covalent bonds, lignin remains in the lignocellulosic complex associated with polysaccharides, especially hemicellulose. Lignin cleavage into macromolecules causes depolymerization of biomass and exposes the structural chain of hemicellulose and cellulose, facilitating access to hydrolysis of these polysaccharides [75–78]. Under optimized process conditions, it is possible to remove lignin without causing severe disruption of the monosaccharides of interest from cellulose and hemicellulose. In processes with dilute acid applied at high temperatures, the system is influenced by the thermal process that results in pore opening in the biomass structure; cleavage of the structure is performed by acid as the chemical catalyst of the process [50].

Application of acids in the pretreatment process is a widely explored technique, with established industrial processes; there nevertheless remains a need for improvements aimed at cost reductions, lower generation of process inhibitors, higher yields, less degradation of essential compounds in the production system, lower reagent consumption, and reduction of environmental impacts.

3.2.3   Oxidizers

Oxidative pretreatment techniques are performed using agents such as hydrogen peroxide (H_2O_2), ozone, and oxygen, involving processes with high yield in biomass delignification. These techniques are associated with electrophilic substitution processes, chemical bond displacement, alkyl-aryl ether bond cleavage, and/or aromatic ring cleavage [4, 50, 79].

Oxidative processes occur because of the high reactivity of these oxidizing agents to aromatic rings. They have a direct effect on lignin structure, and they consequently access the hemicellulose structure of the lignocellulosic complex. Because there is no selectivity, for the chemical structure of lignin, these oxidizing compounds can aggressively attack hemicellulose and cellulose, causing loss of valuable compounds to the downstream process; therefore, strict control in use of this technique is essential [4, 50].

Hydrogen peroxide is a widely applied oxidizing agent for this technique and has great potential for pretreatment of biomass, mainly because it leaves no residue in the material as it degrades in oxygen and water [79, 80]. Even so, its lack of selectivity can lead to high concentrations of inhibitors from lignin and hemicellulose [50].

The H_2O_2 delignification potential is related to the release of hydroxyl ions and superoxides released by reagent degradation at pH 11.5–11.6, a range determined by Gould [81], who demonstrated that at pH less than 10 and greater than 12.5, there is no efficiency in the pretreatment process of lignocellulosic biomass by H_2O_2.

The mechanism of action of H_2O_2 in lignocellulosic biomass is the result of the presence of hydroxyl ions and superoxides released in the degradation of H_2O_2 that have high reactivity, resulting in the immediate cleavage of bonds with low energy activation in the lignocellulosic complex, resulting in mass loss of the structure [4, 35, 79]. The H_2O_2 concentration should be greater than 1%, and the reagent-to-biomass

ratio should be 0.25 for good yields [81]. In addition to the loss of lignin by cleavage resulting from the release of reagent ions, cleavage of the hemicellulosic structure was reported for pretreatment of lignocellulosic biomass by H_2O_2 and solid with high cellulose percentage [80].

Wet oxidation is an oxidative pretreatment technique where oxygen is injected into the liquid phase under high temperatures (120–325 °C) and high pressures (0.5–20 MPa) to increase oxygen solubility and velocity of reaction, leading to contact biomass oxidation, resulting in the formation of organic salts, simple biodegradable compounds, or complete oxidation forming carbon dioxide and water [4, 82–86]. The reaction mechanism of the wet oxidation process in relation to biomass is generally explained by free radical chain reactions in the system and/or by reaction pathways based on self-catalysis by the release of intermediate products of structure degradation of biomass such as acetic acid and formic acid [84, 87, 88].

Ozonolysis is a promising oxidative pretreatment technique based on the use of ozone to reduce biomass recalcitrance. It is widely studied for bleaching processes in the pulp industry and for wastewater treatment, and it is currently gaining prominence as an alternative for pretreatment of lignocellulosic biomass [89]. The ozonolysis technique is considered green because ozone is a powerful oxidant with high oxidation potential in contact with biomass and when decomposed forms oxygen and can be safely released into the environment; the system is run at environmental temperatures and pressures [90, 91].

Ozone is highly reactive to lignin; however, like other oxidative reagents, it has low selectivity and can react with carbohydrates and other compounds, causing degradation of products of interest to the downstream reaction system [89]. The reaction between ozone and lignocellulosic biomass is thought to be mediated by mechanisms involving C–C bonds and cleavage of aromatic centers and glycosidic bonds [89, 92]. High ozone reactivity is a result of electron deficiency in a terminal molecule during resonance, directly affecting compounds with high electron density (C–C bonds and aromatic rings), resulting in attack on lignin and carbohydrate structures [89, 91, 93]. Travaini et al. [94] studied sugarcane biomass pretreated with ozone and reported partial attack of insoluble lignin, transforming it into soluble lignin, with loss of total lignin, and demonstrating the efficiency of delignification in ozonolysis process.

The application of this technique has advantages such as low generation of inhibitory compounds and low degradation of hemicellulose and cellulose under mild and mild operating conditions. Usually, ozone is produced and used on site, reducing the need for reagent transport. Furthermore, there is no need for the addition of chemical catalysts; this reduces pollution by depleting residual ozone as oxygen. By contrast, ozone has exothermic characteristics that may require a cooling system; it is highly reactive, flammable, and corrosive, requiring resistant materials for reactor construction [89].

3.2.4 Ionic Liquids

Ionic liquids (ILs) are pure salts with low melting points (<100 °C), composed of organic cations and organic or inorganic anions. ILs with melting points below room temperature are known as ionic liquids. Most ILs are non-flammable and have low or negligible vapor pressure, chemical, and thermal stability, and their physical properties can be adjusted for a specific task by varying the cation and anion amounts [95].

There are several types of ILs, including acidic ionic liquids (AILs) that turn can be subdivided into Lewis acidic ionic liquids (LAILs) and Bronsted acidic ionic liquids (BAILs) [96]; protic ionic liquids [97], and dicationic ionic liquids [95].

The mechanism of action of ILs in biomass usually involves lignin attack, dissolving it by the deconstruction of the lignocellulosic matrix by breaking the bonds between the basic units. Lignin consists of seven different types of linkage bonds, including β-O-4, α-O-4, β-5, 5-5, 4-O-5, β-1, and β-β. However, the β-O-4 bond accounts for between 50 and 60% of total bonds. During cleavage of the β-O-4 bond, an intermediate β-1 interlock is formed prior to further degradation, while the β-5 bond is converted to stilbene. Stilbene is a comparatively non-reactive and colorless compound initially present in lignin that is insoluble in water and has mainly two isomers [95].

According to molecular dynamics simulations, the interaction between ILs and biomass depends to a large extent on IL solubility [98]. Lignin degradation performance through ILs depends on solvation parameters, as predicted by the Kamlet–Taft solubility model. The model is widely used to predict three empirical parameters of IL polarity in biomass pretreatment: hydrogen-bond acidity, hydrogen-bond basicity, and dipolarity/polarity [99].

Because of their low vapor pressure, ILs are thought to be green alternatives to volatile organic solvents. ILs that contain anions with high hydrogen-bond basicity such as chloride, phosphates, phosphonates, and carboxylates are excellent solvents for cellulose dissolution [100]. They also have high potential for energy-efficient biomass pretreatment, recyclability, and various properties that can be adjusted to the product that needs to be obtained. Some liquids can be prepared from renewable biomass raw materials [95]. One of their disadvantages is that liquids can become more viscous in pretreatment processing, making them difficult to use and opening up their operational processes [101]. Anther difficultly with pretreatment with ionic liquids is that the largest of these is toxic to cellulase and should be removed prior to subjecting the biomass to enzymatic hydrolysis [102].

Pretreatment of lignocellulosic biomass generally involves heating the dry and milling biomass to moderate temperatures, containing the excess ionic liquid in question, such that the LI can be recycled later. These pretreatment processes must be further refined, modified, optimized, and expanded. This process has been studied for many years [100].

Studies have reported successes in biomass pretreatment experiments using IL. Da Costa Lopes et al. [101] reported that lignin content and cellulose crystallinity decreased significantly when wheat straw was treated with 1-ethyl-3-methylimidazole acetate. Monosaccharide yield increased to 81–97%, and the liquid has been reused more than 20 times. The fractionation of completely dissolved wheat straw materials led to cellulose-rich and hemicellulose-rich components. Pretreatment also produced high-purity lignin [103].

Semerci and Güler [97] investigated IL 1-butylimidazolium hydrogen sulfate (HBIMHSO$_4$) as pretreatment of cotton stalks. They used 20% (m m^{-1}) of water and 15% (m m^{-1}) of biomass at 120 °C for four hours. Pretreatment resulted in significant structural changes in biomass. The lignin content of cotton stalks was reduced by 35%, and the cellulose content increased from 36 to 55%. Enzymatic hydrolysis of biomass increased almost fivefold despite an increase in biomass crystallinity. Morphological changes in cotton stalks observed using SEM analysis revealed differences in composition and enzymatic accessibility of biomass samples subjected to pretreatment.

3.2.5 Organosolv

The pretreatment technique using organosolv has applications for many compounds including methanol, ethanol, acetic acid, peracetic acid, and acetone, being mixed in water and exposed to biomass. This technique is notable for high yields in the removal of lignin and hemicellulose from lignocellulosic complexes, generating substances of high purity as well as keeping the cellulose solid and relatively intact [104].

The action of organosolv in lignocellulosic biomass pretreatment processes occurs through the separation of the lignocellulosic complex in the cleavage of internal lignin and hemicellulose bonds that are isolated in low-molecular-weight fragments and generally dissolved in the supernatant. Cellulose maintains solid structure susceptible to hydrolysis processes [77, 105]. The process of removing lignin and hemicellulose structure increases pore volume in biomass and surface area and reduces recalcitrance [105].

Biomass pretreatment with organosolv is a promising technique for the generation of high-purity, low-molecular-weight lignin and xylose polymers. This structural fractionation is directly related to the effects of solvent property on delignification and precipitation. The use of organosolv in process integration concepts is compelling because it generates purity by-products that can be used for various purposes [104, 105]. Organosolv has high economic value; therefore, the use of the pretreatment technique depends on the reagent recovery processes, usually performed by distillation and recycling to the system, considerably increasing energy consumption and requiring high throughput at this stage to make the technique viable [104]. Another obstacle to the application of the technique is the need for extreme rigor to avoid solvent volatilization owing to the high flammability potential of these substances [77, 104].

To reduce the energy consumption of the operation of this technique, some investigators addressed the addition of a catalyst, usually an inorganic acid, to improve the delignification process and to increase the efficiency of the technique [77, 104, 106]. The technique was applied at high temperatures (>185 °C), where the release of organic acids from the structures is believed to act as a catalyst in the process of rupture and stabilization of lignin macromolecules [107]. In this context, it is understood that the pretreatment process with organosolv can be evaluated in three fractions, the lignin fraction, the solubilized hemicellulose fraction, and the solid medium cellulose fraction.

The most commonly used organosolv in pretreatment techniques are alcohols, mainly methanol and ethanol, because of their low boiling point, facilitating the recovery process and generating low acquisition costs. High-boiling alcohols were also studied, although they require high energy consumption for recovery. Other compounds such as organosolv (e.g., formic acid and acetic acid), organic peracids (e.g., peracetic acid and pericetic acid), cetone (e.g., acetone), and others such as dioxane, phenol, and ethylenediamine have also been applied in the technique [104, 106, 107].

The mechanism of pretreatment with organosolv is the result of three chemical reactions: (1) degradation of lignin and hemicellulose by cleavage of internal bonds of ether, ester, and 4-O-methylglucuronic acid ester bonds; (2) disruption of the glycosidic bonds of hemicellulose and the amorphous regions of cellulose, this process being dependent on the solvent and the conditions applied to the pretreatment; (3) under severe conditions, mono- and oligosaccharides are dehydrated in HMF and furfural, or in acids such as levulinic and formic, followed by condensation between lignin and reactive aldehydes [104, 108–110]. In pretreatments using organosolv, the swelling of the crystalline cellulose region has been reported, increasing the surface area of this structure and facilitating hydrolysis [106, 111].

Pretreatment with organosolv is a process of removal of lignin and hemicellulose by solvation and solubilization of compounds. Selective cleavages of the structures of the lignocellulosic complex are the most efficient mechanisms within this technique, as well as the generation of compounds with high purity. However, because the biomass to which pretreatment is applied varies in terms of source and composition, and because solvents that can be used for pretreatment are also diverse, further investigation is required as to the behavior of the mechanism of action, the technique, and the delignification process [104].

Organosolv pretreatment is still considered a technique with high economic costs. Nevertheless, within current concepts of the circular economy and biorefineries, this technique can provide high added-value by-products and may be considered for integration and optimization of processes, making the use of organosolv a promising technique for pretreatment of various biomasses.

3.2.6 Thermochemicals

Thermochemical pretreatment is a technique used to modify biomass properties in the presence of catalysts. Thermochemical pretreatment techniques include supercritical CO_2 and ammonia fiber explosion (AFEX).

Among pretreatment processes using supercritical fluids, carbon dioxide (CO_2) stands out for its high performance in chemical structure compound extraction processes, because it is non-flammable and toxic, recoverable, low cost, and inert, in addition to presenting safer critical pressure and temperature conditions than other solvents [112, 113].

The supercritical point is reached when the temperature and pressure applied to the system are higher than the critical values, such that the fluid can be considered an expanded liquid or a compressed gas [114]. CO_2 has a critical point in temperature of 304.2 K and a critical pressure of 7.38 MPa, and at this point, it has near liquid density and near gas viscosity [112]. The biomass moisture has a positive influence on the supercritical CO_2 process, being responsible for good yields in hemicellulose partial hydrolysis reactions. This is because wet biomass in contact with supercritical CO_2 dissociates hydrogen bonds of microfibrils of hemicellulose and cellulose, resulting in increased accessibility and contact surface. Water present in biomass under supercritical conditions causes biomass swelling, facilitating deeper access of CO_2 molecules to the biomass structure and increasing reaction yield. Subsequently, an explosive release of pressure occurs and supercritical CO_2 breaks the biomass fibers, reducing structure recalcitrance [113, 115–117].

AFEX is a technology that utilizes high pressure (e.g., 250–300 psi) and moderate temperature (e.g., 90–100 °C) associated with chemical catalyst (ammonia) to increase accessibility to the biomass structure [118]. The action mechanism of this technique is based on the cleavage of lignocellulosic complex bonds through structural modifications in the biomass cell wall, gradually increasing the internal pores of the biomass and solubilizing the structures of the lignocellulosic complex. Two reactions occur simultaneously, ammonolysis and hydrolysis, converting acetyl and ester bonds into amines and organic acids [119, 120]. A major advantage of AFEX is that nitrogenous residues serve as an important source of nitrogen in biological processes that may be of interest to the system [121]. AFEX reduces lignin recalcitrance and promotes partial depolymerization of hemicellulose and decrystallization of cellulose [118].

3.3 Biological

Biological pretreatments offer a potential alternative to ensure the unlocking of complex lignin structures and thereby enabling access to sugars and products of interest [122]. Access may be possible through lignolytic enzymes that are capable of disrupting complex lignin structures and making energy-bearing organic carbons accessible

[122]. The by-products produced during the biological pretreatment stage generally do not affect subsequent hydrolytic processes, because the pretreatment conditions are generally mild. Furthermore, in this process, the use of chemicals is not involved, and there is no need for recycling of chemicals in the final phase of the process [123]. However, some of the greatest challenges to be overcome in this type of model are the high cost (application of special enzyme) and the time. Other disadvantages such as substantial loss of holocellulose (cellulose and hemicellulose) and scale-up (reactor design and decontamination) also need to be addressed to make an industrial application viable [124].

Chen et al. [122] found that white-rot fungi were the most effective microorganism model of lignin degradation. For biofuel production, these microorganisms are preferred for fungal pretreatment because they ensure highly delignified cellulose-rich biomass. The mechanism of degradation is mainly associated with the action of enzymes through oxidative processes such as laccases (benzenediol oxygen oxidoreductase, EC 1.10.3.2) and various types of peroxidases (lignin peroxidases (LiPs; EC 1.11.1.14), manganese peroxidases (MnPs; EC 1.11.1.13), versatile peroxidases (VPs; E.C.1.11.1.16), and manganese-independent peroxidases (MiPs; EC 1.11.1.7)) [122, 125, 126]. In addition to these enzymes, some low-molecular-weight metabolites may also be associated with lignin biodegradation, including chemical oxidizing agents and natural mediators of ligninolytic enzymes [127, 128].

Lignin peroxidases are known for the oxidative capacity of high potential redox aromatic rings, including compounds such as veratryl (3,4-dimethoxybenzyl) alcohol, methoxybenzenes, and non-phenolic lignin model dimers. For this enzyme, non-phenolic aromatic substrates are preferred [126]. It has also been seen that oxidation of phenolic compounds may be possible with the presence of veratryl alcohol that provides a cation radical to act as a redox mediator [129, 130].

Manganese peroxidases act on both phenolic and non-phenolic lignin units through lipid peroxidation reactions [131]. The mechanism of action is associated with the oxidation of Mn^{2+} to Mn^{3+} that oxidizes phenol rings to phenoxy radicals, thereby leading to decomposition of compounds [123].

Lignin peroxidase and manganese peroxidase are the two main supporting enzymes acting on the lignolytic system. Both are heme-containing glycoproteins that require hydrogen peroxide as an oxidizing agent. Some of the fungi that produce them are *Phanerochaete chrysosporium, Pycnoporus cinnabarinus, Ceriporiala cerata, Ceriporiopsis subvermispora, Cyathus stercoreus,* and *Pleurotus ostreatus* [123, 132].

Laccases are another class of enzymes that have effects on lignin. Catalysis is associated with the oxidation of phenolic units of lignin and phenolic compounds and aromatic amines to radical. The action of laccases on this material, together with lignin peroxidase and manganese peroxidase, may lead to complete degradation of lignin. However, they also require a redox mediator for potential effects on lignocellulosic materials such as 3-hydroxyanthranilic acid, 2,2-β-azino-bis (3-ethylthiazoline-6-sulfonate) [123].

Studies reported promising effects with an 82% increase in hydrolysis rate with the use of white-rot fungus *Irpex lacteus* after 28 days of pretreatment on corn stalks.

The effect of this significant increase was associated with the variety of extracellular, hydrolytic, and oxidative enzymes produced by the fungus during pretreatment. Such enzymes and other metabolites left in pretreated corn stalks could also continue to play important roles during material hydrolysis at later stages [133].

In general, the use of fungi during biological pretreatment is a suitable option for the delignification processes. Nevertheless, their slow growth, lasting for several weeks or months, is the principle disadvantages of fungal pretreatment: the issue of time and loss of holocellulose previously reported. The use of enzymes for direct treatment of biomass is an encouraging alternative to overcome such challenges. The action of enzymes during the process is closely associated with the mechanism for each of them as described above; however, in this case, they are not produced by microorganisms in the same system.

Factors such as temperature, pH and enzyme concentration are important during enzyme pretreatment. Ramos et al. [134] tested the effect of crude enzymatic extract of *P. chrysosporium* on sugarcane bagasse for mechanical pulp production. They found that crude enzyme extracts (containing lignin peroxidase, manganese peroxidase, and laccase) were more advantageous than pretreatments using fungi. In this system, 36 h of enzymatic pretreatment with H_2O_2 addition resulted in a higher pulp yield than fungal pretreatment for two weeks.

In some cases, it has been shown that pretreatment with crude extracts resulted in a synergistic action of various enzymes on the substrate [135, 136]. For example, enzymatic pretreatment of wheat straw with lignolytics (laccase and peroxidase) and cellulolytics (carboxymethylcellulase (CMCase) and avicelase) contributed to an in vitro degradation of wheat straw cell walls [136]. Nevertheless, further studies are needed to examine the influence and characteristics of various types of enzymes, as well as their interactions with the substrate, when mixed in the biological pretreatment of biomasses.

3.4 Combined Pretreatments

In general, pretreatment methods aim to intensify the results of subsequent steps, including hydrolysis of biomass to produce fermentable sugars, among others.

Combined pretreatments, such as grinding, screening, use of dilute aqueous ammonia and ultrasound have been employed on lignocellulosic biomass, including corn cob, sorghum stalk, and corn husk. The biomass was ground and sieved in 20–40 mesh, ammonia was added at 1.0–4.0% and the samples were inserted in a 90 W and 59 kHz ultrasonic processor where the temperature was maintained at 40–70 °C for 1–4 h. The crystallinity of the samples was monitored in their crude form and pretreated using an X-ray diffractometer, and surface analyses were observed using scanning electron microscopy (see Session 2.2). In corn husks, alkaline pretreatment was positive and the concentration of 2.0%, 60 °C and intermediate time of 2 h obtained the highest sugar yields; however, the removal of lignin and hemicellulose was very low. For the corn cob and sorghum stalk, the trend was the same as

those of pretreatments, because lignin and hemicellulose contents decreased when the combination of ultrasound and alkaline treatment was used, improving the sugar yield, that is, coupled with increased contact surface between biomass and hydrolyzing enzymes, an effect linked to ultrasound. Electron micrographs demonstrated the effect of pretreatment, because the raw biomass appears compactly, and after treatment, it has a rough and looser surface, suggesting that parts of the hemicellulose and lignin were removed during the process [137].

In term of industrial-scale processes, the application of wood chips for power generation presents a promising logic, especially when it comes to constant charge flows. The benefits and limitations of this technology were evaluated using ultrasonic pretreatment, and its effectiveness was tested as the physical characteristics of biomass (SEM, see Sect. 2.2.4.1) and bio-oil yield. Waste from a pulp and paper mill was milled on a 5-mm grid and subjected to an ultrasonic bath ($250\,W\,L^{-1}$) with a capacity of 34 L, and the wood chip biomass treatment was carried out under the following conditions: 0.5 h and 170 kHz followed by 1.5 h to 40 kHz with power of 1000 W and maximum temperature of 76 °C [138]. From the analysis of biomass morphology by scanning electron microscopy, it was observed that the treated wood presented openings in its surface and no chemical or inhibitor formation was observed during the process. More specifically, ultrasound treatment improved the accessibility and caused small erosions on the surface of the particles, improving heat and mass transfer rates, favoring the subsequent processes of use of this biomass, and enhancing the yield. Nevertheless, in this type and treatment, attention must be paid to factors such as exposure time and energy invested, as they can degrade the material to the point of making it non-usable for the process.

The use of combined pretreatment technologies presents the essence of the possibility of positively developing the expected result. Generally, there is a synergistic effect aiming to pretreat substrates with high efficiency; for example, the combination of ultrasound and alkaline and acidic treatment techniques is compelling for the disintegration of organic particles and improving their solubilization [139].

Studies aimed at improving the efficiency of anaerobic digestion for biogas production have focused on the combination of chemical and microwave pretreatments. The addition of a chemical compound (sodium citrate) initially disintegrates the structure of biomass and the input of energy provided by the microwaves facilitates the solubilization of organic matter; consequently, the synergy between the pretreatments helps permeabilize the biomass. The yield was considerably higher when combining treatment techniques, proving the beneficial effect of these processes acting together [140].

In similar fashion, studies have combined NaOH with ultrasonic treatment to accelerate biomass biodegradability [141]. To study effective waste management in the cosmetic industry, investigators combined thermo-alkaline, thermo-sonication, and thermo-alkaline-sonication treatments. Combined treatment with thermo-alkaline-sonication showed higher degradation value (66.1%) of biomass and favored methane production by 50%, increasing energy consumption by only 1.1% [142].

The choice of the appropriate pretreatment methodology considers several factors such as biomass characteristics and their potential application in biotechnological processes, especially with respect to cost reduction and development of environmentally viable processes, as well as the generation of products with added value, according to the principles of circular economy.

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