



Pretreatment methods of lignocellulosic wastes into value-added products: recent advances and possibilities

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Abstract

A number of industries currently produce many tons of agroindustrial wastes with significant consequences on the environment and human and animal health. In recent years, increasing emphasis has been placed on reducing this negative impact. This review article aims to investigate the use of pretreatment methods that can be applied as an alternative to the usage of residual biomass. In addition, we seek to highlight the efficiency of the processes as well as possible weaknesses, which are associated with high energy and reagent consumption, low yields, and possible secondary impacts. Generally, the waste chemical composition consists mainly of cellulose, hemicellulose, and lignin; these can be fractionated, extracted, and purified to produce different value-added products, such as biofuels, organic acids, enzymes, biopolymers, and chemical additives. Despite the multiple possibilities to produce different products from lignocellulosic biomass, further research is still required to enhance the efficiency of the methods used nowadays and find new procedures.

Keywords Agroindustrial wastes · Biomass · Cellulose · Lignin · Hemicellulose

1 Introduction

Agricultural activities can lead to multiple waste accumulation and environmental pollution. Both consequences derive from factors such as the practice of industrial activities and compound usage that are intended to optimize and improve agroindustrial outputs [1]. Agroindustrial wastes produced around the world constitute, annually, a large amount of waste material (approximately 37,522,440,479 kg in 2017) [2]. These should be fulfilled by an appropriate pretreatment

process, in order to avoid adverse effects against the environment, human, and animal health. However, most of the agroindustrial wastes around the world do not receive adequate post-treatment and end up being incinerated or disposed in makeshift landfills [3].

Within the last decades, numerous promising studies have been made, aiming to develop and improve agroindustrial wastes disposal methods designed for the obtainment of value-added products [4]. One of the most prominent types of wastes is that of lignocellulosic nature [5, 6]. Lignocellulosic biomass is generally composed of a complex mixture of cellulose, hemicellulose, and lignin; therefore, for the efficient use of its components, it is necessary to carry out adequate separation processes. Due to the high amount of matter present within the lignocellulosic biomass, an agroindustrial separation process is not common. With the purpose of obtaining acceptable yields in the components, additional pretreatment steps are generally required [7–11]. During the pretreatment stage, the natural characteristics of lignocellulosic compound bonds are modified by altering the supramolecular structures. This makes the pretreatment stage essential to enhance the depolymerization of the structural components in subsequent treatments, increasing the degradability by using biological, physical, and chemical methods

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[12]. Once said step is performed, it is possible to obtain the constituent components [7]. Different subproducts can be obtained, which can have a wide application range, categorized in bioenergy, biomaterials, chemical precursors, enzymes, among others.

The different value-added products obtained after a pretreatment process offer several benefits in comparison with those that have not been pretreated, such as environmental, net energy gain, and economical aspects [13–16]. These indicators can be a growth opportunity for local farmer communities, employment opportunities, industry sector, and energy sectors [17]. These advantages account for a pretreatment process to be a very promising and feasible technology.

In order to provide a better understanding and vision, this work has involved a comprehensive review of the current pretreatment methods for lignocellulosic wastes from agroindustrial activities, for obtaining value-added products. The first section describes specific data on agricultural production and its residues around the world, as well as the problems related to the accumulation of this type of waste. In the second section, we present the chemical composition of the constituents of lignocellulosic material. Consequently, the third section describes a review of the current pretreatment methods for lignocellulosic material that has been carried out. Finally, the last section of this work contains a review of some of the possible products from pretreated lignocellulosic wastes, empathizing the industrial, energetic, and economic importance of this biomass.

2 Agroindustrial production around the world

Worldwide, numerous hectares of land are used for agricultural use (Table 1). In addition, a wide variety of products are generated (Table 2). As a result of the large production of agricultural products around the world, large quantities of

Table 1 Agricultural land usage in hectares around different areas of the world to 2016 [18]

Regions	Hectares (1000 ha)
East Asia	648,396.00
South America	620,418.50
North America	468,778.91
Europe	464,405.37
Oceania	384,051.44
West Asia	272,272.41
North Africa	174,298.63
Central Africa	166,274.70
South Africa	165,090.60
Central America	124,152.50

agroindustrial wastes are inevitably generated, many of which are lignocellulosic in nature (Table 3).

3 Problems related to agroindustrial activity

Agroindustrial activities have caused a series of problems associated with the environment and human and animal health. Related to the environment, the soil is one of the major sources of pollution and degradation by these activities. Agricultural activities have been linked to soil erosion [29]. This effect can have consequences such as sedimentation, soil fertility loss, and agricultural production decrease, which make agricultural activities unsustainable [30]. Moreover, the most direct effect of soil erosion is sedimentation. Water runoff and excessive sedimentation contribute to the degradation of soil and water bodies [31]. Additionally, components with nitrogen, phosphorus, organic compounds, and heavy metals of pesticides can reach aquifer mantles and bodies of water, causing the intoxication of aquatic life and eutrophication of water [32].

Nowadays, the consequences generated by the accumulation of pesticides and fertilizers used during agroindustrial harvests can contribute to a damaging impact on human health. Therefore, it is necessary to improve the efficiency of agroindustrial processes in order to reduce their environmental impact [33, 34]. Adverse effects may depend on the routes and exposure time, and health conditions of the individual [35]. The most representative damages to human health are dermatological, respiratory, gastrointestinal, carcinogenic, and reproductive and endocrine affections [33, 35]. In European areas, there are taxes denominated as landfill taxes that seek to avoid the accumulation of wastes. This trend is currently expanding to other countries [36]. Moreover, there is a current trend in developed countries to consider by-products of industrial processes as recyclable materials, rather than considering them as wastes. There are currently numerous companies that no longer consider these by-products as wastes, but rather as raw materials that can be used for other processes [27].

4 Agroindustrial waste composition

Agroindustrial wastes of lignocellulosic nature are mostly composed of different structural fractions (Table 4) that can be extracted and applied for the synthesis of different products and materials because of their high energy content [43].

Table 2 Production of common agricultural products by continent to 2016 (index 2004–2006 = 100) [18]

Continent	Crops	Cereals	Vegetable oil	Roots	Fruits and vegetables	Sugar
Africa	134	132	142	133	132	115
America	131	131	158	99	113	150
Asia	136	124	147	131	151	132
Europa	115	119	148	97	109	103
Oceania	110	90	161	107	107	89

4.1 Cellulose

Plants are responsible for producing many tons of cellulose per year [44]. This makes cellulose the most abundant natural polymer in the world, making it and its derivatives one of the most prolific research topics [45]. Consequently, cellulose-based products and applications are abundant. They are harmless to the environment due to their capacity to easily return to the carbon cycle through a degradation process, in the presence of decomposing organisms [46]. Cellulose is typically differentiated for being a biodegradable compound; having good mechanical properties; being biocompatible, non-toxic, and poorly soluble in water; and having a broad susceptibility to being chemically modified [47]. It is a syndiotactic homopolymer with a molecular formula of $(C_6H_{10}O_5)_n$, composed of D-anhydroglucopyranose units (glucose units). The glucose units are combined together by means of β -(1-4)-glucosidic bonds forming a dimer called cellobiose, which is the fundamental unit of cellulose [48]. Hydroxy groups (OH) in the structure of D-anhydroglucopyranose, the primary (C6) and the two secondary (C2 and C3), exhibit different polarities, making them able to be involved in intramolecular and intermolecular hydrogen bond interactions [49].

Cellulose can be considered as an isotactic polymer of cellobiose (Fig. 1) [46, 48] Among the most common cellulose applications, there are uses such as an additive for adhesives, paper-based products, drilling fluids,

Table 3 Types of agroindustrial waste and its production in different parts of the world

Waste	Production (MT/year)	Location	Reference
Rice straw	740.95	Worldwide	[10]
Wheat stalk	529.00	Worldwide	[19]
Corn bagasse	384.80	USA	[20]
Sugar beet	274.20	Worldwide	[18]
Sugarcane bagasse	166.40	Brazil	[21]
Soy stalk	143.50	Worldwide	[22, 23]
Sawdust	64.05	USA	[24]
Cotton stalk	24.82	Worldwide	[25]
Orange peel	15.00	Worldwide	[26]
Barley straw	0.00083103	Europe	[27, 28]

cement-based materials, food coatings, and catalysis support structures, and wide applications in biomedicine [45].

4.2 Lignin

Lignin is one of the three major components of plant organic matter and represents the main natural aromatic source [50]. Lignin has aromatic units instead of the long carbon chains presented by cellulose and hemicellulose. Its chemical characterization depends on the type of vegetal and extraction method [51]. Lignin is a compound with different types of phenols, such as coniferyl, p-comaryl or hydroxyphenyl alcohols, and sinapyl; the first one predominates in softwoods, while the latter ones are present in a greater proportion in hardwoods. These monomers are united by carbon-oxygen bonds between the β -termination of the propenyl group (β -O-4) and half of the p-hydroxy [52] (Fig. 2).

Due to the complexity of its chemical structure, molecular weight is an important parameter. The molecular weight of lignin ranges from 1000 to 20.000 $g\ mol^{-1}$, and it is fragmented into subunits that are repeated randomly. This contributes to a more difficult extraction process, making lignin analysis constantly complex [53, 54].

Major applications of lignin include using it as a copolymer in plastics, reinforcement additive in polymeric compounds, adhesives, flocculants, antioxidant coating in the food industry, precursor for the manufacture of carbon fibers, and components in batteries for energy storage, and in biomedical applications [55].

4.3 Hemicellulose

Hemicelluloses are heterogeneous polymers formed by pentoses (xylose and arabinose), hexoses (mannose, glucose, and galactose), and various acidic sugars. The ratio and proportion of these compounds vary between different types of plant species [56]. Hemicellulose polysaccharides can be easily volatilized or hydrolyzed by a dilute acid or base and are highly soluble in alkaline media. Consequently, hemicellulose, unlike cellulose, is removable with alkaline solutions from the plant cell walls [57]. Due to their structural variability, hemicelluloses can be divided into four classes: xylanes,

Table 4 Biochemical composition of common agroindustrial wastes

Residue	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Rice straw	41.0–57.0	8.0–19.0	33.0	[37]
Rice husk	25–35	18–21	26–31	[38]
Wheat stalk	34.0	27.6	18.0	[39]
Corn bagasse	42.4	29.6	21.7	[40]
Sugar beet	26.0	28.0	4.5	[39]
Sugarcane bagasse	33.6	29.0	18.5	[39]
Soy stalk	38.0	16.0	16.0	[39]
Sawdust	47.5	22.5	30.0	[39]
Cotton stalk	42.0	12.0	15.0	[39]
Orange peel	9.2	10.5	-	[41]
Barley straw	32.5	25.7	23.0	[39]
Miscanthus straw	44.7	29.6	21.0	[39]
Spent coffee	49.8	9.5	22.1	[39]
Pineapple bran	30	36	7	[39]
Banana peel bran	12.1	10.2	2.9	[42]

manoproteins, β -glucans with mixed bonds, and xyloglycans (Fig. 3) [58].

Generally, the concept of hemicelluloses refers to all those polysaccharides in the cell wall that cannot be characterized as celluloses or pectins [59]. Among the applications of hemicellulose, there are its uses in biomedical and pharmaceutical β -glucans applications, as reinforcement additive in biomedical polymers, as adhesives, and as flocculants [58, 60–62].

5 Pretreatment methods for lignocellulosic agroindustrial wastes

5.1 Chemical methods

5.1.1 Acid pretreatment

Acid pretreatments of lignocellulosic biomass have several advantages. Within them, there are acid solutions that can remove lignin and hemicellulose without any previous treatment, and it is a low-cost method [63, 64]. Various types of mineral acids can be used, with sulfuric acid and hydrochloric acid being the most used. These are usually applied under

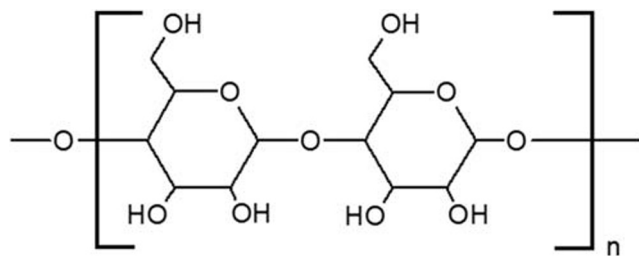


Fig. 1 Cellulose structure

different conditions of concentration, temperature, and time, depending on the kind of waste. Overall, high temperatures, long reaction periods, and high concentrations usually decrease the yield, as well as the crystallinity and thermal stability of cellulose [65, 66]. In spite of its effectiveness, acid pretreatment has the disadvantage that toxic compounds such as furfural; HMF; and acids, such as acetic, formic, levulinic and fungal, can be released as well as aliphatic and phenolic groups, due to the degradation of sugars and lignin, respectively [67, 68].

In a study conducted by McIntosh et al. [69], the laboratory and pilot capacity of diluted acid as a pretreatment method was evaluated in combination with the steam explosion technique to treat *Eucalyptus grandis* tree samples for later hydrolysis, in order to produce bioethanol. At the laboratory scale, the digestibility of glucans and glucose yield was 68.0% and 51.3% respectively, for the pretreated biomass at 190 °C for 15 min at 4.8 wt% H_2SO_4 . At the pilot level, the pretreatment is at 180 °C for 15 min at 2.4 wt% H_2SO_4 , followed by steam explosion that led to glucans digestibility yields and glucose yields of 71.8% and 63.6% respectively.

5.1.2 Alkaline pretreatment

Alkaline pretreatments have several advantages, especially the fact that it is a method that uses less aggressive reagents, compared with those used in acid pretreatments such as sulfuric acid [70]. Also, alkaline pretreatments are effective in the delignification of the biomass, without significantly affecting its cellulosic structure [4].

The use of reagents such as sodium hydroxide, sodium carbonate, ammonia, and calcium hydroxide is common for

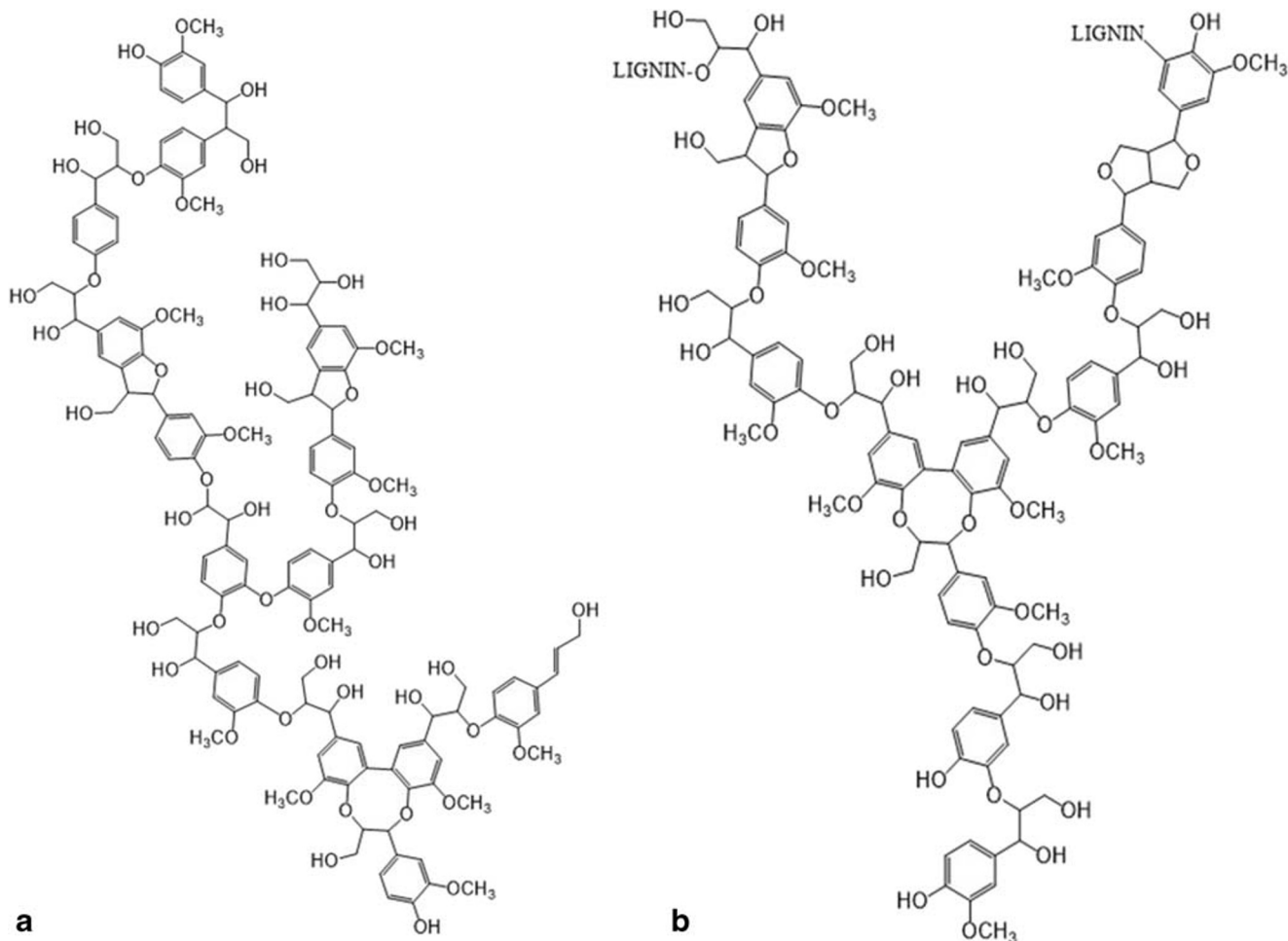


Fig. 2 Chemical structure of lignin in softwood. Coniferyl alcohol (a). P-comaril alcohol (b)

alkaline methods [70]. During the pretreatment process, there are reactions that include the dissolution of lignin and hemicellulose, and the de-esterification of intermolecular ester bonds. This kind of pretreatment removes substitutions of acetyl and uronic acids present in the hemicellulose that would otherwise reduce subsequent accessibility of enzymes to hemicellulose and cellulose [71]. The degree of polymerization of the components is also altered, causing changes in surface area, porosity, and crystallinity of the treated solids [72].

Mittal et al. [73] performed an analysis of the hydrogen peroxide loading during an alkaline pretreatment to separate the lignin from the polysaccharides present in corn stover. The influence of peroxide was examined in a range of 30–500-mg H₂O₂/g stubble of dried corn at 50 °C for 3 h, obtaining that at 250-mg H₂O₂/g dry corn stubble, the delignification was approximately 80%.

5.1.3 Ionic liquids pretreatment

Ionic liquids are composed of organic heterocyclic cations and several anions. These are non-volatile, non-flammable, and

can exist in liquid state within a wide range of temperatures, the most common being below 100 °C. Imidazole ion salts are currently one of the most popular ionic liquids for pretreatment processes [74]. Its usage is due to its effectiveness in dissolving cellulose. The general mechanism consists of the alteration of the hydrogen bonds that crosslink the lignocellulose, which increases the biomass digestion. Then, using solvents such as water, ethanol, or acetone, it is possible to recover the cellulose fraction; however, it is a method that requires high investment costs [63, 65, 75].

Yamada et al. [76] evaluated the use of an ionic liquid pretreatment in bagasse, for the subsequent use of the biomass in a direct ethanol fermentation by using cellulase-displaying yeast. The results showed that 1-butyl-3-methylimidazolium acetate was the most effective ionic liquid among those studied. After pretreatment, direct fermentation obtained a yield of 73.4% after a 96-h fermentation.

5.1.4 Organic solvent pretreatment

Pretreatment with organic solvents is applied to isolate lignin as a solid material and carbohydrates as a syrup,

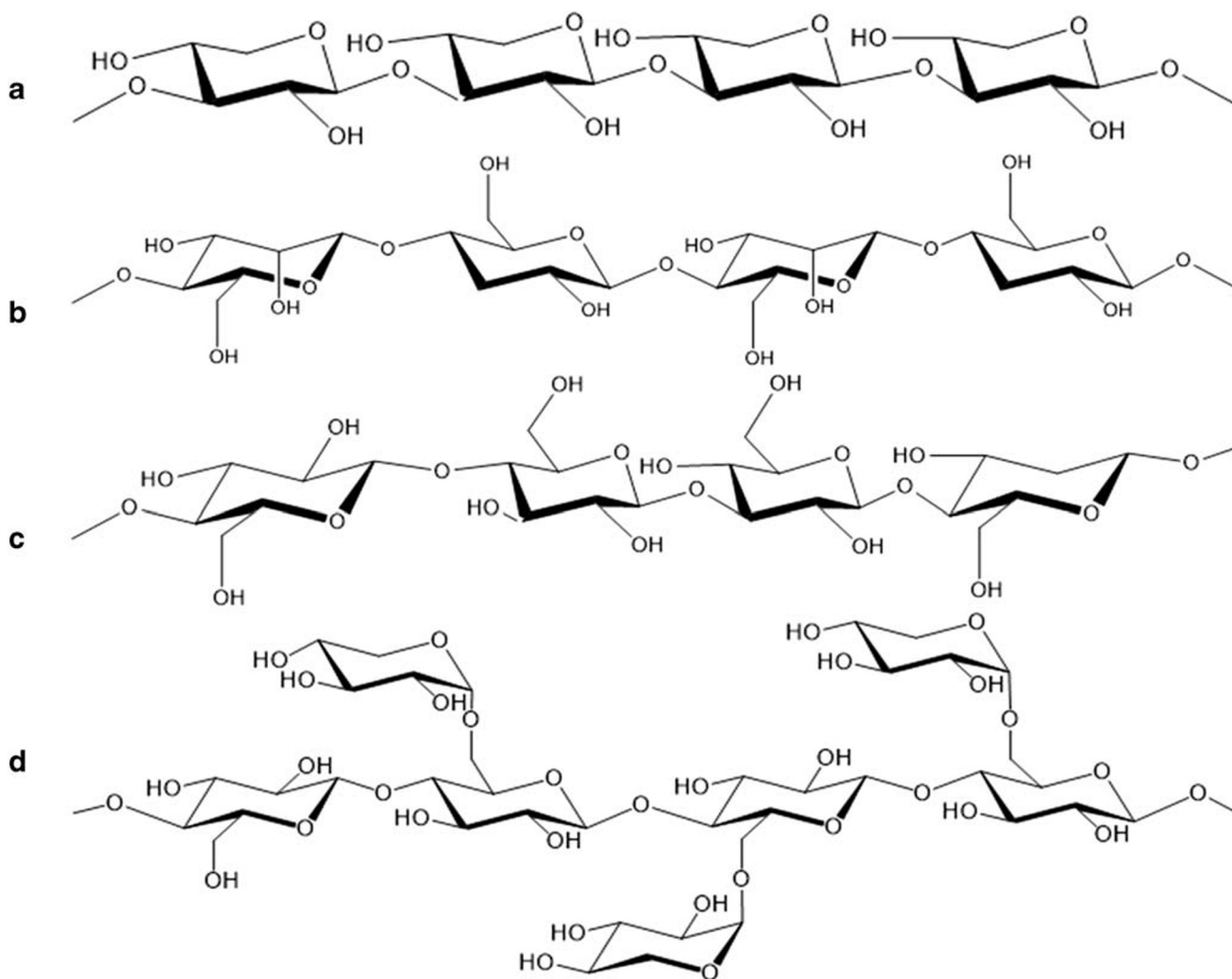


Fig. 3 Primary structure of xylanes (a), manoproteins (b), β -glucans with mixed bonds (c), and xyloglucans (d)

which is beneficial, since both are raw materials for numerous products [77]. Normally, this type of pretreatment is performed using a strong inorganic acid as a catalyst to hydrolyze the bonds shown in lignin. The main advantage of an organic solvent pretreatment is that it provides easy recovery of the organic solvent by distillation for a recycled use [78].

Salapa et al. [79] evaluated the efficiency of an organic solvent pretreatment over wheat straw at different temperatures and times, using five different organosolvents (ethanol, methanol, butanol, acetone, and diethylene glycol), in the presence of 23 mol/m³ of sulfuric acid as catalytic for a later ethanol production. After the subsequent enzymatic digestion, the highest ethanol production yield was 67%, which was obtained under conditions of 180 °C for 40 min of pretreatment. In addition, pretreatment with diethylene glycol at 160 °C for 40 min also showed good results due to its ethanol production yield of 65%.

5.2 Physical pretreatment methods

5.2.1 Milling

The purpose of this technique is to reduce the particle size and to promote the disruption of the lignocellulosic material crystallinity. The method provides a reduction of the raw material that ranges between 0.2 and 2.0 mm, which increases the specific surface area for a subsequent hydrolysis process [80]. This method affords the advantage of severely reducing the processing time. In addition, it decreases the amount of water consumed; however, it maintains the limitation of requiring high energy consumption [63].

In a study led by Q. Liu et al. [81], the sugar recovery capacity of a two-stage corn stover pretreatment was evaluated. The first stage being a dilute HCl pretreatment, and the second involving a wet grinding technique. The optimum conditions were obtained at a temperature of 120 °C for 40 min for the pretreatment with 0.7% HCl, and 15 min during the

wet mill pretreatment. At these conditions, the xylose yield was 81% and 64% for glucose.

5.2.2 Sonication

The sonication technique is based on the application of ultrasonic waves through a fluid to promote pressure variations [82]. Acoustic waves generate microcavities in which gas bubbles grow and then collapse, generating shock waves that cause mechanical effects, such as particle erosion and a consequent particle size reduction [83].

In a study done by Song et al. [84], a sonication pretreatment process was accomplished on roasted wheat straw, in order to obtain biomass pellets for later use as biofuel. The results showed that with the assistance of sonication, pellets of a higher quality than those obtained at the same pressure with no ultrasonic vibrations can be obtained.

5.2.3 Extrusion

The extrusion pretreatment method consists of the operation of generating objects with a defined cross-sectional profile by means of forcing them through a mold with the desired transversal size. The material generally undergoes expansion when it leaves the mold [85]. The process can be affected by variables such as the screw extruder profile, the extrusion speed, and the system temperature [86].

Extrusion methods have different effects on biomass, such as reduction of particle size distribution, increase in specific surface area, changes in crystallinity, and visible changes in biomass structure. It is generally common for the extrusion method to be combined with other chemical methods such as alkaline or acid treatments, aiming to improve the process efficiency [87].

In a study carried out by Oliva et al. [88], an extrusion pretreatment process on barley straw was evaluated. The study combined the steam explosion and extrusion techniques for an optimal fractionation of the lignocellulosic material. The process had a yield of 84%, 91%, and 87% in the recovery of glucans, hemicellulose, and lignin, respectively.

5.3 Physical-chemical pretreatment methods

5.3.1 Steam explosion

Steam explosion is a hydrothermal pretreatment in which the biomass is rapidly heated in a reactor containing saturated steam at high pressures, 0.69–4.83 MPa, in a temperature range between 160 and 260 °C. The time period in which the biomass remains in the reactor varies from seconds to several minutes [89].

During this process, the vapor condenses and penetrates the biomass, initiating an autohydrolysis where the glycosidic

hemicellulose bonds are broken due to the organic acids that are generated from the acetyl groups present in this component. This results in subsequent solubilization of the hemicellulose, causing a mechanical disruption in the lignocellulosic matrix [90]. Therefore, this technique is usually used to alter the plant structure, solubilize hemicellulose, and promote rising in the accessible specific surface area of the lignocellulosic material, by enzymes or other compounds. This technique has the advantage of being environmentally friendly; nevertheless, it is still a developing technology, because of the need to improve the design of reactors, the mode of operation, and the mixture of catalysts that can improve the biomass pretreatment effectiveness [91, 92].

Medina et al. [93] studied the effect of steam explosion pretreatment over palm oil empty fruit bunches. Optimal pretreatment results were obtained at a temperature of 195 °C for 6 min. Pretreated biomass showed a 34.69% increase in glycan content and a 68.12% reduction in hemicellulose content. In addition, the increase in the subsequent enzymatic digestion yield was 33%.

5.3.2 Hot water pretreatment

The hot water pretreatment for lignocellulosic biomass keeps liquid water at temperatures between 140 and 240 °C. During the pretreatment, the hemicellulose is depolymerized and the products dissolve in the liquid phase, while the cellulose is completely retained in the solid phase. The temperature of the water causes lignin to suffer from simultaneous depolymerizations and polymerizations, due to its glass transition temperature in aqueous conditions (between 80 and 100 °C) [94]; insoluble lignin is retained in solid waste [95].

This technique has advantages that include the unnecessary use of chemical additives, the non-requirement of using a corrosion-resistant reactor, and the formation of low toxicity compounds [96].

In a study conducted by Mohan et al. [97], the ability to obtain total reducing sugars by means of hot water pretreatment applied over bamboo samples was evaluated. For this, the reaction times were varied between 5 and 40 min, and the temperature between 170 and 220 °C. The results showed that the highest yield of 42.21% was obtained at a temperature of 180 °C for 25 min.

5.3.3 Supercritical CO₂ explosion

Supercritical CO₂ is characterized for being considered as a green solvent because of its non-flammability and non-emission of organic vapors. Its critical temperature (T_c) is 31 °C, and its critical pressure (P_c) is 1071 psi [98]. After the pretreatment, the solvent can be easily separated. Process variables such as temperature, pressure, extraction bed size, and solvent flow, among others can be modified to maximize

yields on specific compounds. In addition, the combined use of this method with others such as sonication and extrusion is common [99]. The explosive release of CO₂ after the pretreatment process breaks the biomass cellulose and hemicellulose structures, increasing the surface area for eventual hydrolysis [100].

In a study developed by M. Jiao Zhao et al. [101], agroindustrial wastes including corn stover, corn cob, and sorghum stalk, all with a moisture percentage of around 75%, underwent a long supercritical CO₂ pretreatment between 12 and 60 h, at low temperatures (50–80 °C) and pressures between 17.5 and 25.0 MPa. The results showed that in the subsequent enzymatic hydrolysis of the lignocellulosic material, the yield of sugars was 3 to 4 times higher than those obtained for the material that had not received a supercritical CO₂ pretreatment.

5.3.4 Ammonia fiber expansion (AFEX™)

The expansion with ammonia fiber is a pretreatment that applies anhydrous or gaseous liquid ammonia in a pressurized container to treat lignocellulosic materials [102]. One of the advantages of this technique is that the ammonia can be reused by a gas recycling system integrated into the main system used [103].

The addition of ammonia under high pressures and temperatures promotes the decrystallization of cellulose, depolymerization of hemicellulose, and deacetylation of acetyl groups. These changes dramatically increase subsequent enzymatic hydrolysis stages, leading to high yields for pretreated biomass by ammonium fiber expansion [104].

In a study carried out by Perez-Pimienta et al. [105], the response of agave bagasse to a pretreatment with ammonia fiber expansion was evaluated. Results showed that the method preserved all the carbohydrates present in the biomass samples, and in subsequent hydrolysis, the yield of sugar production (glucose and xylose) was 42.5%.

5.3.5 Plasma

Pretreatment with plasma uses ozone (O₃) for the degradation of the lignin present in lignocellulosic biomass to optimize a subsequent hydrolysis process [106].

Plasma is capable of generating highly reactive compounds such as hydroxyl radical (HO^{*}) and hydrogen peroxide (H₂O₂), which are capable of degrading cellulose to obtain glucose [78]. Therefore, the pretreatment is capable of breaking the complex structure of lignocellulosic materials, leading to their eventual bleaching and delignification [107].

Ravindran et al. [108] used non-thermal plasma technology to pre-treat brewer spent grains. Variables such as voltage (22, 25, and 28 kV), solvent (acid, basic, and water), and time (5, 10, and 15 min) were taken into account. After a further

hydrolysis stage, the best-reducing sugar yield was obtained for the biomass pretreated for 10 min in water at 28 kV. The results showed that 162.9-mg/g brewer spent grain was obtained for the pretreated material, while 75.94 mg/g was obtained for the control.

5.3.6 Microwave pretreatment

This type of pretreatment focuses on irradiating lignocellulosic materials with microwaves [109]. They accelerate chemical, biological, and physical processes due to heat and wide collisions caused by the vibration of polar molecules and movement of ions [110].

The microwave pretreatment performance is highly dependent on the dielectric properties of the lignocellulosic material to be treated. The loss tangent (ratio of the dielectric loss factor to the dielectric constant of the material) is normally calculated to measure the net efficiency of the microwave pretreatment [111, 112].

In a study conducted by Zhu et al. [113], acid (H₂SO₄) and basic (NaOH) pretreatments assisted by microwave were performed on sugarcane bagasse. The results showed that the microwave-assisted pretreatment was more effective than those pretreatments that used conventional heating methods. Yields for reducing sugars were 4 times higher for the microwave-assisted method and performed in 5.7 times less time.

5.4 Biological pretreatment methods

5.4.1 Microbial consortia

Microbial consortia are complex communities with a high diversity of microorganisms that interact in numerous ways, either cooperatively or competitively. In some cases, these communities often carry out activities that cannot be performed by a single microbe. Microbial consortium applications offer several advantages such as functional robustness, efficient productivity, and high stability when biochemically degrading a substrate [114, 115]. However, this technique has the disadvantage that biomass degradation rates and physico-chemical transformation of lignocellulose are easily affected by several factors, such as physical (temperature, aeration, substrate size), chemical (pH, residue composition, enzyme activity), and biological (species of microorganisms and the interaction between them) factors [116]. The microorganisms that are normally used include bacteria *Cellulomonas* and *Cytophaga*, and many fungi, such as *Humicola*, *Penicillium*, *Aspergillus*, and *Trichoderma*, the last being one of the most studied for its ability to secrete large amounts of extracellular protein [117].

Brethauer and Studer [118] applied a microbial consortium that included the fungi *Trichoderma reesei*, *Saccharomyces*

cerevisiae, and *Scheffersomyces stipitis* in order to produce ethanol using wheat straw as substrate; the results showed that there was a yield of 67% in the production of ethanol, showing that the technique used has a high potential as a versatile and economical process for the generation of products based on lignocellulosic biomass.

5.4.2 Use of fungal species

Fungi are characterized for being a heterotrophic species and having cell walls composed of chitin. There are fungal species such as white rot, brown rot, and soft rot, which are characterized for their ability to degrade different components present in lignocellulosic biomass. This technique has the advantage that it does not require extensive use of chemical reagents or high energy consumption; however, at an industrial level, it has the disadvantage that it requires long incubation times [119, 120].

White rot fungal are characterized by their ability to degrade lignin through enzymatic complexes that include a wide variety of cellulolytic and ligninolytic enzymes [121, 122]. Brown rot fungi differ by their ability to degrade the cellulose and hemicellulose contained in biomass by means of hydrogen peroxide, endoglucanases, and β -glucosidases [119]. Soft rot fungi have the ability to degrade cellulose due to them possessing a wide range of cellulolytic enzymes such as endo-1,4-glucanase, exo-1,4- β -glucanase, and 1,4- β -glucosidase [119]. In addition, they are capable of degrading lignin to a lesser extent, due to the presence of enzymes such as lacases [119, 123].

Dhiman et al. [124] used a fungal consortium (*Pholiota adiposa* and *Armillaria gemina*) in order to produce enzymes to perform a pretreatment over wet rice straw and wet sauce that later underwent enzymatic hydrolysis and conversion to bioethanol. The results obtained showed that the yields obtained in the hydrolysis of the pretreated biomass were 74.2% and 63.6% for the rice straw and the sauce respectively. The good yield was confirmed later, by converting the hydrolyzate into bioethanol with a yield of 72.4%.

5.4.3 Enzymatic pretreatment

Cellulose can be used as a source of carbon for the development of a wide range of living organisms including fungi, protists, bacteria, and plants; these organisms can transform cellulose through cellulases, a synergistic enzyme complex that facilitates the hydrolysis of cellulose and its subsequent biological conversion to a usable source of energy [9, 125]. This system is mainly composed of three enzymes, called endo- β -1,4-glucanase (EC3.2.1.4), cellobiohydrolase (CBH) (EC3.2.1.91), and β -glucosidase (EC3.2.1.21). These act together to hydrolyze the β -1,4-glycosidic bonds of cellulose to release fermentable sugars [126].

The application of enzymes to degrade lignocellulosic materials has several advantages, such as a reduced capital investment, low energy cost, low reagent dependence, and environmental friendliness, yet it keeps the limitation that it is a process with low industrial profitability since the incubation period is prolonged. In many cases, there is low efficiency in the yields obtained [127, 128].

Ziemiński and Kowalska-Wentel [129] analyzed the co-fermentation of a mixture of sugar beet pulp silage and vinasse (3:1, 1:1, and 1:3 w/v) for the production of biogas. It was found that enzymatic pretreatment with Celustar XL and Agropect pomace of sugar beet pulp silage, before methane fermentation, generated a partial degradation of the biomass polysaccharides, significantly increasing biogas production. The results showed that the highest biogas yield (765.5 mL/g) was obtained from the 3:1 mixtures of sugar beet pulp silage and pretreated vinasse. This had a 27.9% better performance than its non-pretreated counterpart.

6 Generated products and their application in various areas

6.1 Products in the bioenergy area

Currently, there is a growing demand on investigating different lignocellulosic sources of low-cost pretreatment methods and inoculum to produce environmentally friendly fuels (Table 5). This is due to different factors such as the rising cost of conventional fuels, global warming problems related to CO₂ emissions, and production rentability, among others [140]. Usually, the concept of bioenergy refers to any gas, liquid, or solid that was processed by biorefinery technologies; these have a tendency to be used as a renewable energy source. One of the main advantages of biofuels is that their source crop can sequester CO₂ from the atmosphere due to the increased biomass productivity. In total, 17.97 million tons (carbon dioxide-equivalent) accumulative greenhouse gas emission could be mitigated [141]. Crops can be used to produce energy through combustion methods without increasing net CO₂ emissions, due to the CO₂ removed from the atmosphere by the crops themselves during their growth process [13].

Bioethanol and biodiesel are classic examples of this type of energies [140]. However, in the last few years, the conversion of lignocellulosic wastes into biohydrogen is being considered as a promising technology for the replacement of fossil fuels [142]. This is principally because hydrogen production by fermentation is a plausible alternative when compared with other feedstocks, due to lignocellulose abundance and different available pretreatment methods [143]. Biohydrogen could easily be produced from agricultural wastes via fermentation processes [144, 145]. Soltan et al. produced biohydrogen by a

Table 5 Biofuels obtained from various agroindustrial wastes

Residue	Product	Pretreatment method	Inoculum	Reference
Sawdust	Bioethanol	Ionic liquid	<i>Saccharomyces cerevisiae</i>	[130]
Sugarcane bagasse	Bioethanol and biogas	Alcaline	<i>Saccharomyces cerevisiae</i>	[131]
Sugarcane bagasse	Bioethanol	Alcaline and hydrodynamic cavitation	<i>Scheffersomyces stipitis</i>	[132]
Rice straw	Biogas	Alcaline and extrusion	Digested sludge from agroindustrial manure	[133]
Rice straw	Biohydrogen	Enzymatic hydrolysis	<i>Thermoanaerobacterium thermosaccharolyticum</i>	[134]
Barley straw	Biodiesel	Acid	<i>Rhodococcus sp.</i>	[135]
Corn straw	Biodiesel	Alkaline and acid	<i>Mycobacterium smegmatis</i>	[136]
Wheat straw	Biogas	Organosolvents and alkaline	Digested sludge from agroindustrial manure	[137]
Wheat straw	Biohydrogen	Microbial consortium	Digested sludge from agroindustrial manure	[138]
Wheat straw	Biodiesel	Grinding, alkaline, and enzymatic digestion	<i>Trichoderma viride</i>	[139]

multi-fermentation of a complex mix of agroindustrial wastes and achieved a net energy gain of 1.82-kJ/g feedstock. Similarly, Soltan et al. achieved a net energy gain of 32.2 ± 4.2 -kJ/kg feedstock using an integrated fermentation of a mixture of 30:70 metals in mixed fruit peels (MFPS):paper mill sludge (PMS). Besides the production of bioethanol, biodiesel, and biohydrogen, biogases like methane and propane have been generated from lignocellulosic wastes [146, 147]. Dahunsi et al. used an aerobic digestion of peanut hull to produce biomethane and obtained a net energy gain of 303 kWh tons⁻¹ [148]. It has been reported that by 2025, biodiesel production and power generation could amount to 72.11 thousand tons and 1.59 billion kW h respectively. Due to its higher energy recovery, the organic wastewater biogas industry has the highest output and net profit, followed by the waste incineration power generation industry [141]. Panigrahi et al. produced biogas using an electrochemical pretreatment on yard waste followed by an anaerobic digestion and obtained a net energy gain of 4.75-kJ/g volatile solid (VS) [149]. These results suggest that the conversion of lignocellulosic wastes into biofuels can be a promising technology due to the high net energy gain obtained by several studies [15, 16, 149].

6.2 Chemical products and their applications beyond bioenergy

It is possible to obtain a variety of value-added chemical products using the lignocellulosic biomass from agroindustrial wastes as a raw material due to their chemical composition [150] (Table 6). Cellulose degradation generally entails glucose production; meanwhile, hemicellulose depolymerization can be used to produce pentoses like xylose; arabinose; and hexoses, like mannose, glucose, and galactose [49, 56]. A wide variety of aromatic compounds can be obtained from lignin due to its molecular structure being abundant in phenolic structures [162].

Some of the precursor compounds with six carbons in their structure that can be obtained from biomass degradation

processes are citric acid, 5-hydroxymethyl-furfural, lysine, gluconic acid, glucaric acid, and sorbitol. Similarly, for compounds with five carbons, there are itaconic acid, furfural, levulinic acid, glutamine acid, xylonic acid, and arabito. For compounds with four carbons, there are succinic acid, fumaric acid, malic acid, aspartic acid, acetoin, threonine, etc. Among the obtainable precursor compounds with three carbons in their structure, there are glycerol, 3-hydroxypropionate, propionic acid, and malonic acid [163].

The precursor compounds have an inherent possibility of generating a wide range of organic compounds [164]. Organic acids are some of the most relevant value-added products that can be synthesized from the previously mentioned precursor compounds. Some commonly produced organic acids from agroindustrial wastes are acetic acid, oxalic acid, lactic acid, itaconic acid, succinic acid, butyric acid, and propionic acid [163–165].

The production of biochemical compounds such as enzymes, vitamins, hormones, amino acids, and antibiotics from agroindustrial wastes are commonly obtained from microorganisms such as *Aspergillus niger*, *Trichoderma reesei*, *Halomonas sp.*, *Bacillus subtilis*, and *Aspergillus fumigatus* [165, 166]. The industrial enzyme market is one of the most prolific between the different chemical and biochemical compounds that are marketed worldwide. It is projected that by 2023, the market for industrial enzymes should reach \$ 7.0 billion from the value of \$ 5.5 billion reached in 2018 [14].

There is also an uprising interest in the production of carotenoids using different lignocellulosic wastes as feedstock. This is due to the high production cost of these through biotechnological methods. Carotenoids have wide applications as pigments in the food industry and in the pharmaceutical and nutraceutical industries, and as additives in animal feed [167].

Among other compounds that are produced from agroindustrial wastes, there are the chelating agents. These work through bioabsorption mechanisms which are based on a combination of electrostatic attraction mechanisms, complexing processes, ion exchanges, and covalent bond

Table 6 Value-added chemical products obtained from lignocellulosic agroindustrial wastes

Residue	Product	Pretreatment method	Application	Reference
Coconut, cassava, and soya flour	Lycopene	Biologic	Food industry	[151]
Soya stover	Carotenoids	Extrusion and fungal hydrolysis	Pharmaceutical, biotechnological, and chemistry industry	[152, 153]
Wheat bran and corncobs	Fumaric acid and itaconic acid	Fungal hydrolysis	Pharmaceutic and chemistry precursors	[154]
Corncoobs	Furfural	Grinding	Pharmaceutic and chemistry precursors, plastic and polymer industry, refinery	[155]
Rice straw	Lignolytic enzymes	Fungal hydrolysis	Lignocellulosic material treatment	[156]
Wheat rice hay and bran, sugarcane bagasse, peanut peel, birch, and beech branch	Cellulolytic enzymes	Fungal hydrolysis	Lignocellulosic material treatment	[157]
Corn stover	L-Lysine	Acid	Food industry	[158]
Corn stover	Citric acid	Acid	Pharmaceutic, chemistry, food, cosmetic, and agricultural	[159]
Cottonseed meal and corn cob	D-Lactic acid	Hydrolysis without pretreatment	Pharmaceutic, cosmetic, and chemistry	[160]
Corn cob	Succinic acid	Acid	Chemistry, pharmaceuticals, food, cosmetic, and polymeric industry	[161]

forming [168]. Chelating agents can find application in water cleaning, since they can remove heavy metals and dyes through bioabsorption mechanisms [169].

6.3 Material and material additive production

In recent years, lignocellulosic biomass has been attributed with a high potential for obtained value-added materials with a wide range of applications (Table 7), this due to their qualities of being renewable, recyclable, and sustainable; however, they are accused of having an important impact on environmental contamination [140, 183]. Currently, biotechnological advances together with nanotechnology and engineering have generated interest in doing research focused on the use of lignocellulosic biomass for the design of materials that are multifunctional for the bio- and non-bio-sectors of the modern world. This new direction is socially acceptable and commercially viable, and moreover, it possesses an important impact on industrial societies for the development of a sustainable global economy [7]. One of the most representative types of materials obtained from lignocellulosic sources lies in the field of biodegradable polymers. These kinds of materials can reduce oil consumption and help reduce problems caused by plastic contamination, since they are easily degradable in soils and marine environments [164]. When cellulose, hemicellulose, and lignin have been isolated, they can be incorporated into a wide variety of materials. There are three main routes through which polymeric materials can be obtained from lignocellulosic materials. The first route involves the use of biorefinery waste streams or paper industry wastes. The second route refers to direct use

of the biomass cell walls; therefore, cellulose, hemicellulose, and lignin must be isolated to subsequently convert them into final products. The third route is based on hexoses and pentoses obtainment from lignocellulosic materials for their further processing into a wide variety of compounds, additives, and biopolymers [12, 184, 185]. Depending on the methodology, a wide range of compounds can be developed. They include materials such as bacterial cellulose, keratin, polyhydroxyalkanoate (PHA), chitosan, and polylactic acid (PLA), among other synthetic counterparts [164, 186] (Table 7).

7 Conclusions and perspectives

Worldwide, there is currently a problem related to agroindustrial waste generation. This is due to it having a negative impact on the environment. Therefore, the continuous search for alternatives that help mitigate this problem is essential. As discussed above, the main pretreatment methods for lignocellulosic wastes, i.e., chemical, physical, physicochemical, and biological methods, are looking for an efficient transformation of lignocellulosic biomass into value-added products. Several agricultural residues such as rice, sugarcane, soybean, corn, wheat, cotton, pineapple, sorghum, cassava, barley, banana, oil palm, and bean, among other residues from the wood industry, as well as municipal cellulosic solid wastes, could be used as raw materials to produce many different products. However, each technology has its own associated advantages and disadvantages, depending on the source of biomass, the methods used, and the desired final product. The

Table 7 Polymeric materials obtained from lignocellulosic agroindustrial wastes

Residue	Material	Pretreatment method	Applications	Reference
Wood fibers	Cellulose	Extrusion	Fixed installations (bone plates and screws), surgical sutures, plasticulture, and environmental remediation	[170, 171]
Sugarcane bagasse	Cellulose nanocrystals	Steam blast	Polymeric, pharmaceutical, and biomedical industry	[172]
Eucalyptus pulp	Cellulose nanocrystals	No pretreatment performed	Polymeric and pharmaceutical industry and biomedical	[173, 174]
Beech wood	Polycaprolactone reinforced with nanocellulose microfibrils	Grinding and organosolvents	Additive in polymeric industry, biodegradable materials, biomedical implants, and pharmaceutical	[175, 176]
Ryegrass	PHA	Surfactants	Biomedics, food industry, and adhesives	[177]
Poplar waste	PHA	Hot water	Biomedics, food industry, and adhesives	[178]
Corn stover	PHA	Grinding and alkaline	Biomedical, food industry, and adhesives	[179]
Rice straw	Chitosan	Acid and organosolvents	Biomedical and pharmaceutical industry	[180]
Pineapple leaves	PLA reinforced with nanocellulose microfibrils	Grinding and alkaline	Biodegradable polymers and food industry	[181]
Wheat straw	PLA reinforced with wheat straw fibrils and polycaprolactone	Alkaline	Biodegradable polymers and food industry	[182]

advantages of the lignocellulosic wastes are that such materials have a great potential to produce biomolecules, chemicals products, and biofuels to address the current energy crisis. Within the bioenergy area, a great potential is suggested for energy production from pretreated biomass, due to the obtainable high net energy gain values. There are substantial prospects for economic growth due to the wide range of chemical and biochemical compounds that are possible to produce after a pretreatment process of lignocellulosic feedstock. The enormous amount of obtainable compounds could directly benefit several different industries (textile, materials, biomedical, pharmaceutical, etc.), in as much as many of those use some of the obtainable value-added products as raw materials. Among the main limitations distinguished from the use of lignocellulosic wastes, there are the excessive use of water, energy consumption, and toxic reagents. In addition, it is important to take into consideration the collection, transport, and handling of lignocellulosic wastes in a cost-effective manner. Despite the multiple possibilities of using lignocellulosic biomass, more research is still required, specially to improve the efficiency of the existent pretreatment methods, reduce the costs associated with the processes, and reduce the production of toxic compounds. Moreover, depending on the geographic locations and season, changes in agroindustrial wastes price and its supply could emerge. This could affect production costs and efficiency of the overall process. Moreover, many literature and preliminary studies are made in a small scale but there is still an enormous gap between the laboratory preliminary results, the pilot scale, and finally, the industrial scale.

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