Journal homepage: www.fia.usv.ro/fiajournal
Journal of Faculty of Food Engineering,
Ştefan cel Mare University of Suceava, Romania
Volume XIX, Issue 3 - 2020, pag. 237 - 259

FOOD AND
ENVIRONMENT
SAFETY

PHYSICAL AND CHEMICAL PRETREATMENTS USED FOR BIOETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS - REVIEW

*** Vasile-Florin URSACHI [1] , Gheorghe GUTT [1]**
[1]*Faculty of Food Engineering, "Ştefan cel Mare" University,*
Suceava, Romania, florin.ursachi@fia.usv.ro
*Corresponding author

Received 27th August 2020, accepted 26st September 2020

Abstract: In the last decade, environmental protection is one of the major challenges. It is necessary to ensure the protection of the environment and the conservation of natural resources, in accordance with the requirements of a sustainable economic and social development. The most important impact of modern human activities is the release of large amounts of different compounds after fossil fuels burning; these compounds are responsible for increasing of greenhouse gases (GHG) concentrations in the atmosphere. The depletion of fossil fuels and necessity to increase energy reserves, especially for the propulsion of transport, contributed to search and use of alternative fuels. Partially or completely substitution of gasoline with bioethanol is an alternative method to reduce GHG emissions. Currently, biofuels (first generation) are produced from sources used to feed the population. The competition food vs. biofuel could be solved if biofuels were obtained from renewable resources such as lignocellulosic biomass (LCB). Second-generation biofuels are obtained from raw materials such as agricultural residues (straws, sugarcane bagasse, corn stalks and cobs) and forestry residues (sawdust, bark, branches, etc.) which do not interfere with global food production. In 2019, the main producers of bioethanol were USA, Brazil and EU which produced about 54%, 30% and 5% respectively of the worldwide bioethanol.

This paper reviews one of the most important steps of bioethanol production which is the pretreatment of LCB. Numerous pretreatments are available, as follows: physical, chemical, physico-chemical, biological and combined pretreatments. The combined pretreatments were found to be more effective when compared to single pretreatments, and there is a wide range of combinations that can be applied in the future.

Keywords: *cellulose, hemicellulose, lignin, pretreatment, bioethanol*

1. Introduction

The term biofuel often refers to liquid or gaseous fuels that are used in the transport sector and are obtained mainly from biomass. The main characteristics of biofuels are related to sustainability, reduction of greenhouse gas emissions, development of economic, social and agricultural sector, and food security [1]. In the last century, increasing of global energy consumption has implicitly led to increasing in CO_2, SO_2 and NO_x emissions due to the burning of fossil fuels which is the main cause of air pollution [2].

The reduction of fossil fuel deposits, but also their negative effects on the environment led to the exploration of alternative energy resources which are environmentally friendly [3,4]. Regarding the sources of bioenergy, lignocellulosic biomass (LCB) is an important raw material that can be used for biofuels production and also for extraction of high value compounds [5].

Annually, large amounts of LCB are generated, and these include forest, agricultural and agro-industrial residues that can be capitalized in bioethanol production [6].

The most important polymers present in LCB are cellulose (32% – 51%), hemicellulose (19% – 35%) and lignin (10% – 30%) [7,8]. Compared to agricultural biomass (AB), the physical properties but also the chemical composition of wood biomass (WB) are different. WB has a more pronounced recalcitrance than microbial and enzymatic actions when compared to AB [9].

Currently, critical concerns are focused on the sustainability of bioethanol production, as it is obtained mostly from cereal crops that contain starch and sugar. For this reason, the irrational use of these crops can create competition between food and biofuels [10,11]. The main advantage of lignocellulosic materials (CML) are that they are renewable sources that do not compete with food for human consumption [12-14], thus using these resources may avoid food security issues [6]. Other advantages include the extraction of high value substances [15] and the relatively low cost of processing, which is cheaper than that of crude oil [8,16].

However, LCB also has an important disadvantage that refers to its complex structure, which is resistant to chemical and enzymatic degradation [17]**.** Therefore, in order to modify the physicochemical properties of the lignocellulosic matrix, various pretreatment methods must be applied to the LCB; these pretreatments are considered to be expensive [18-20].

The aim of this review was to identify the physical and chemical methods of pretreatment of LCB and establish which of these pretreatment methods can disrupt the complex structure of LCMs and remove lignin most efficiently. The pretreatment process conditions must to be given special attention because at this step the selection of the best choice can lead to a significant increase in the yield of fermentable sugars and also reduce the formation and release of toxic compounds.

2. Overview of sources and bioethanol production

2.1. Clasification of biofuels

Biofuels are classified into two broad groups: primary and secondary. Primary biofuels are used in crude form for heating, cooking or electricity production. Secondary biofuels are products resulting from biomass processing and can be used for transport or various industrial processes. Depending on the raw material and the technology used for the production of secondary biofuels, they divide into three subgroups: first generation, second generation and third generation (Figure 1) [21-24].

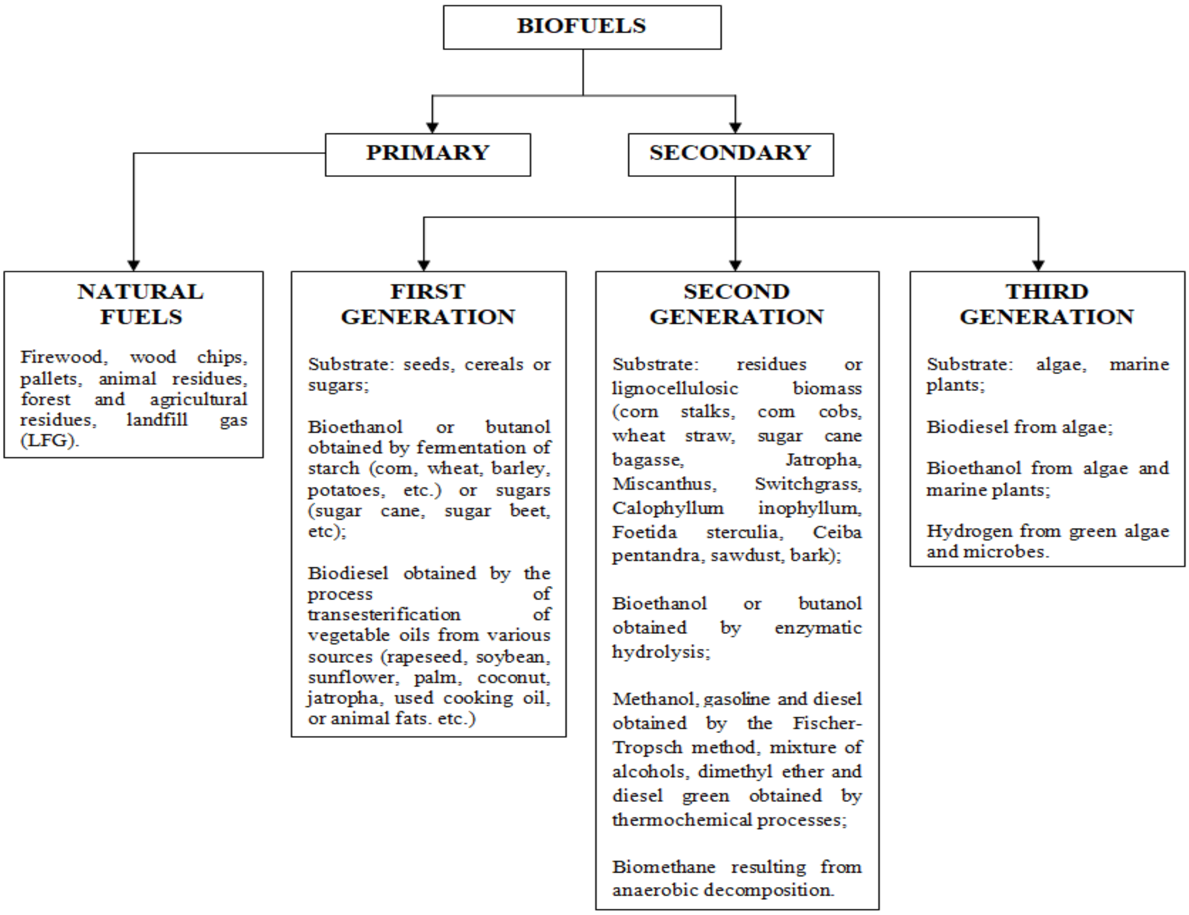
2.2. Global Ethanol Production

Renewable Fuels Association (RFA) argues that the largest worldwide producer of ethanol is the US (corn), followed by Brazil (sugar cane). In 2018, the United States and Brazil produced about 16.1 billion gallons and 7.95 billion gallons, respectively (28%). This means that these two countries produced aproximatively 84% of global ethanol production [25]**.** Figure 2 shows the global ethanol production from 2007 to 2018.

2.3. Structure of lignocellulosic biomass

Cellulose is a linear polymer composed of *D*-glucose units linked by β-1,4 glycosidic bonds. The hydroxyl groups of each glucose unit form intra- and inter-molecular hydrogen bonds and give the cellulose chain a rigid and partially crystalline structure. This crystallinity indicates that the structure of cellulose is more orderly, but limits the action of enzymes during saccharification [27-28].

By removing water from each molecule of glucose, long chains of cellulose that contain 5000 - 10000 units of glucose are formed.



NATURAL FUELS

Firewood, wood chips, pallets, animal residues, forest and agricultural residues, landfill gas (LFG).

FIRST GENERATION

Substrate: seeds, cereals or sugars;

Bioethanol or butanol obtained by fermentation of starch (corn, wheat, barley, potatoes, etc.) or sugars (sugar cane, sugar beet, etc);

Biodiesel obtained by the process of transesterification of vegetable oils from various sources (rapeseed, soybean, sunflower, palm, coconut, jatropha, used cooking oil, or animal fats. etc.)

SECOND GENERATION

Substrate: residues or lignocellulosic biomass (corn stalks, corn cobs, wheat straw, sugar cane bagasse, Jatropha, Miscanthus, Switchgrass, Calophyllum inophyllum, Foetida sterculia, Ceiba pentandra, sawdust, bark);

Bioethanol or butanol obtained by enzymatic hydrolysis;

Methanol, gasoline and diesel obtained by the Fischer-Tropsch method, mixture of alcohols, dimethyl ether and diesel green obtained by thermochemical processes;

Biomethane resulting from anaerobic decomposition.

THIRD GENERATION

Substrate: algae, marine plants;

Biodiesel from algae;

Bioethanol from algae and marine plants;

Hydrogen from green algae and microbes.

Fig 1. Clasification of biofuels [21-24]

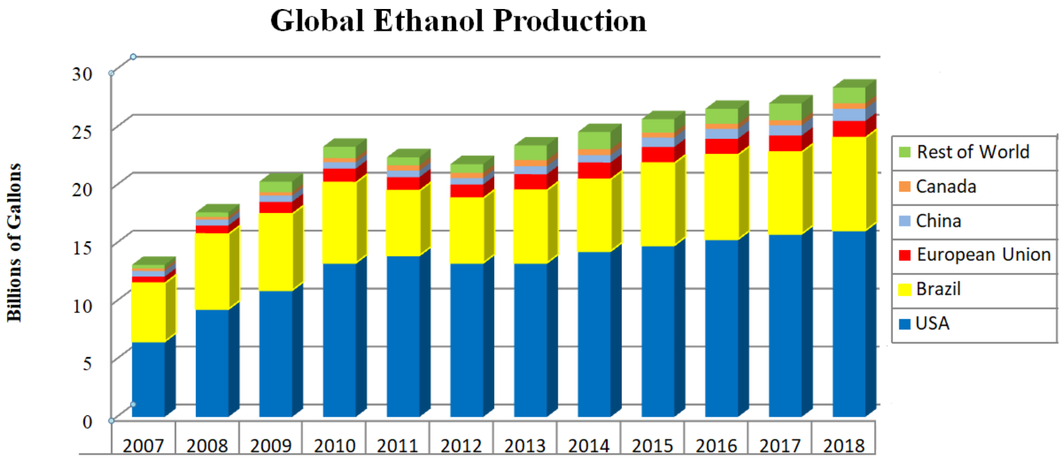


Fig 2. Global Ethanol Production [26]

The basic unit of cellulose consists of two units of anhydrous glucose, also called cellobiose units [29].

Hemicellulose is a carbohydrate that contains different types of sugars: with 5 carbon atoms (β-*D*-xylose, α-*L*-arabinose and rhamnose) and with 6 carbon atoms (β-*D*-glucose, β-*D*-mannose and α-*D*-galactose [30]**.**

Lignin is the second most abundant biopolymer of LCB, after cellulose. In combination with hemicellulose it is distributed around the cellulose fibers in both the primary and secondary cell walls. Lignin has three basic monomers: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [31]**.** Figure 3 shows the structure of LCB. The chemical composition of LCMs used for production of second-generation bioethanol is shown in Table 1.

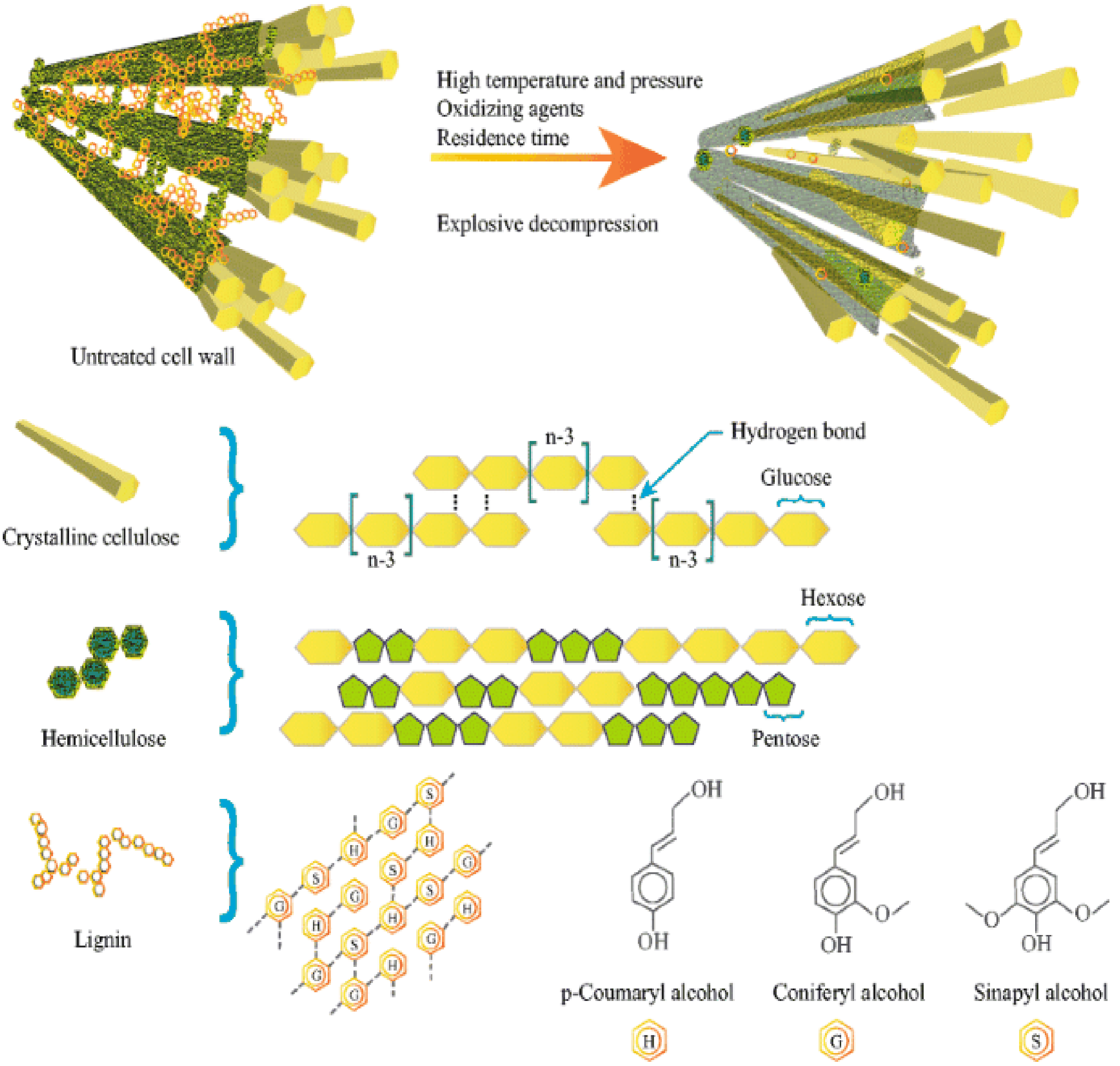


Fig 3. Structure of LCB [32]

Table 1

The chemical composition of LCMs

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractable substances (%)	Ash (%)	References
Agricultural biomass/residues						
Corn stalks	38.0	26.0	18.5	6.0	5.1	[33]
Corn cobs	36.75 ± 0.54	29.98 ± 3.60	23.13 ± 3.40	6.76 ± 1.52	0.95 ± 0.03	[34]
Wheat straws	43.1	27.7	17.5	5.5	5.3	[35]
Rice straws	35.63%	18.06%	31.97%	n.a	10.24%	[36]
Barley straws	33.25	20.36	17.13	5.64	2.18	[37]
Rye straws	35.8	14.5	3.5	n.a	n.a	[38]
Triticale straws	33	23	29	n.a	3	[39]
Oat straws	37.60	23.34	12.85	7.11	2.19	[37]
Sorghum straws	35.87	26.04	7.52	n.a	n.a	[40]
Sugarcane bagasse	45.5 ± 1.1	27.0 ± 0.8	21.1 ± 0.9	2.2 ± 0.1	4.6 ± 0.3	[41]
Rapeseed	37.0	19.6	18.0	19.7	5.7%	[42]
Canola straws	42.39	16.41	14.15	7.56	2.10	[37]
Cotton stalks	31.1	10.7	27.9	9.0	6.0	[43]
Hemp	74	18	13	n.a	n.a	[44]
Hemp fiber	56.1 - 58.7	10.9 - 14.2	6	-	4.3	[45]
Kenaf	31 – 57	21.5 – 23	15 – 19	n.a	n.a	[46]
Jute	72	13	13	n.a	n.a	[44]
Sisal	73	13	11	n.a	n.a	
Grape stalks	16.7 ± 0.2 - 18.0 ± 0.2	2.6 - 5.7	19.2 - 24.2 ± 0.5	22.6	n.a	[47]
Nut shells	25 – 30	25 – 30	30 – 40	n.a	n.a	[48,49]
Coconut	33.29 ± 0.09	33.61± 0.07	19.87 ± 0.08	1.27± 0.05	5.5± 0.05	[50]
Coir	43	<1	45	n.a	n.a	[44]
Banana waste	13.2	14.8	14	n.a	n.a	[51]
Grasses						
Miscanthus	41.9	20.6	23.4	3.7	3.0	[52]
Switch grass	34.6- 45	23.5 - 31.4	12.0-21.0		20.9	[49,53]
Forestry biomass/ residues						
Hardwoods						
Quercus robur	48–49	18–22	29–34	n.a	n.a	[54]
Fagus sylvatica	47–48	18–22	30–35	n.a	n.a	
Populus tremula	48–49	21–25	26–31	n.a	n.a	
Eucalyptus gigantea	49	23	22	n.a	n.a	[55,56]
Alnus rubra	44	30	24	n.a	n.a	

Softwoods						
Picea abies	42	20	27	n.a	8	[39]
Abies alba	35–37	24–26	37–41	n.a	n.a	[54]
Tillia cordata	48–51	20–22	27–32	n.a	n.a	
Salix	37.1	17.8	27.0	3.8	1.1	[52]
Larix occidentalis	48	17	27	n.a.	n.a.	[55,56]
Pinus sylvestris	32.5 - 50	24 - 39.7	16.3 - 20	n.a.	n.a.	[57,58]
Pseudotsuga menziesii	44.0	11.0	27.0	n.a.	n.a.	[58]
Other residues						
Newspaper	0-55	25-40	18-30	5-8	n.a.	[48,59,60]
Waste papers from chemical pulps	60-70	10-20	5-10	n.a.	2	

n.a. – not analyzed

3. The impact of pretreatments on LCMs

The pretreatment step has an important role in the biofuel production process because by pretreating LCB there can be obtained yields of up to 90% as compared to 20% in the case of untreated LCB. [61]**.** The pretreatment step was introduced to separate LCB into the main constituent biopolymers and to facilitate hidrolysis. The pretreatment step should allow an easy recovery of lignin and other non-fermentable constituents that can be used for the synthesis of other chemical compounds [62,63]**.** The pretreatment methods used for bioethanol production from LCB are shown in Figure 4.

3.1. Physical methods for pretreatment of LCB

Physical pretreatments include processes such as mechanical, pressure, microwave, ultrasonication, pyrolysis, pulsed electric field, etc.

3.1.1. Mechanical pretreatment

Mechanical pretreatments of LCB include chipping, grinding and milling. These methods are used for releasing biomass fragments with small particle size, disruption of cell structure, decreasing the crystallinity of cellulose in biomass, and to facilitate further chemical and biological treatments [64]. For raw materials, a certain pretreatment method is required to minimize substrate degradation and improve carbohydrates yield [61,63]. Grinding biomass facilitates the access of enzymes and steam. The energy consumed to reduce the particle size represents approximately 30% of the total energy consumption of the process. The extractable substances can be removed using steam (~160 °C) [61]**.**
Mechanical pretreatment of LCMs is an important step in the technological process of obtaining biofuels because it contributes to improving bioconversion by reducing cellulose crystallinity, particle size, degree of polymerization [65], particle density and

distribution, while increasing enzymatic accessibility and transformation of LCMs. [66]. LCM has a complex composition, thus different types of mills are used to decompose and reduce its crystallinity. The most common types of mills are ball mills, centrifugal mills, colloidal mills, hammer mills, knife mills, pin mills and vibratory mills [67]. Milling is used to reduce the crystallinity and size of LCB particles and can result in particles with a size of 0.2 mm [68].

Mani et al. [69] used a hammer mill with a screen opening of 0.8 mm, 1.6 mm and 3.2 mm and determined the specific energy consumption for grinding wheat straws, barley straws, corn stover and switchgrass that had a humidity of 8.3 – 12.1 %wb, 6.9 – 12.0 %wb, 6.2 – 12.0 %wb and 8.0 – 12.0 %wb, respectively. The average specific energy consumption for wheat straws, barley straws, corn stover and switchgrass was 11.36±1.02 – 51.55±2.93 (kWh t^{-1}), 13.79±0.18 – 99.49±7.35 (kWh t^{-1}), 6.96±0.75 – 34.30±1.47 and 23.84±0.63 – 62.55±0.63 (kWh t^{-1}), respectively [69]. Bitra et al. [70] directly measured the mechanical energy used by the knife mill to reduce the size of switchgrass, wheat straw and corn stover. In the case of the knife mill, for a screen size of 25.4 mm and an optimum speed of 250 rpm, the optimum feed speed obtained was 7.6, 5.8 and 4.5 kg/min, the corresponding total specific energies were 7.57, 10.53, and 8.87 kWh/Mg, and the efficient specific energies were 1.27, 1.50 and 0.24 kWh/Mg for switchgrass, wheat straw and corn stover, respectively. Energy use ratios were determinated and were, as follows: 16.8%, 14.3% and 2.8% for switchgrass, wheat straw and corn stover, respectively [70].

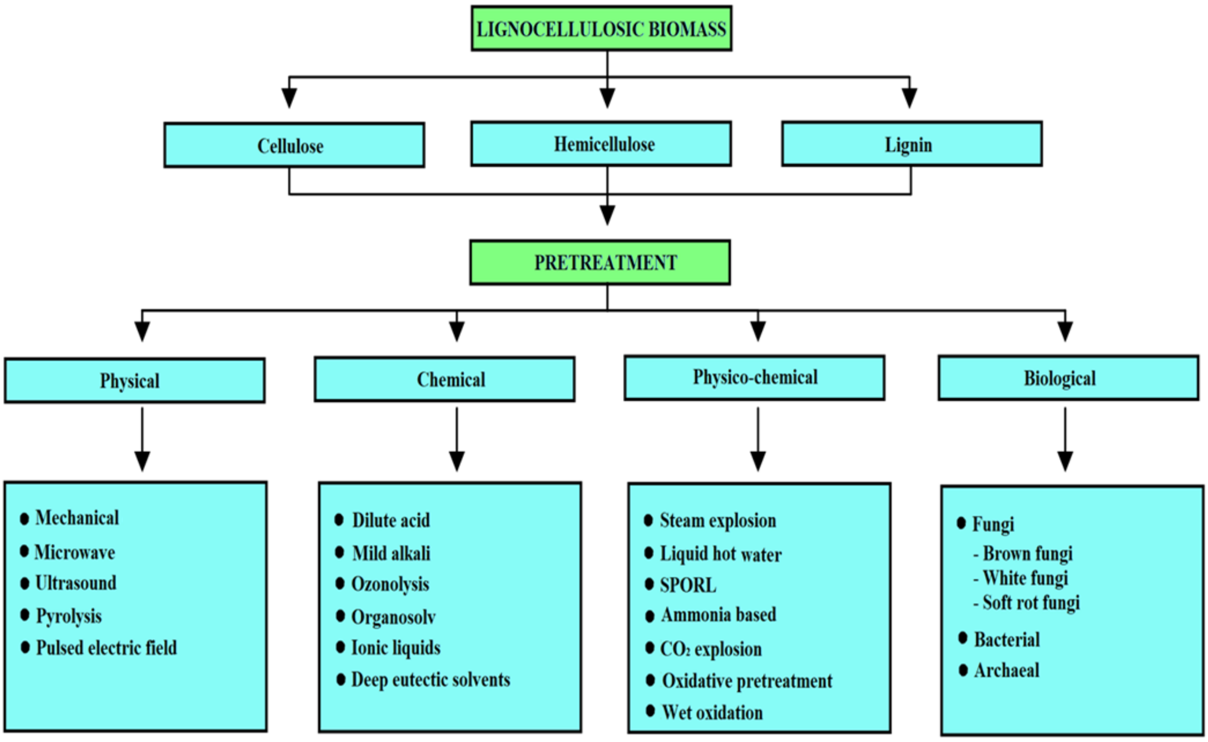


Fig. 4. Pretreatments applied to LCB [49,68,71].

3.1.2. Microwave pretreatment

Microwave irradiation is considered an alternative method to conventional heating [72] and present interest in different domains. The use of microwave irradiation has some advantages such as reduced process energy requirements, uniform and selective processing and the ability to start and interrupt the process instantly [73]**.** There are numerous studies that have shown that microwave irradiation could contribute to the disruption of the complex structure of LCMs [74] and facilitate their enzymatic hydrolysis [75]**.** Combined pretreatments (microwave irradiation + chemical pretreatment) can also be applied to LCMs, and can contribute to the acceleration of the chemical reaction rate [76]**.** Also, microwave irradiation reduces time, and the severity of liquid ionic and alkali pretreatment [77,78].

Ma et al. [79] pretreated the rice straws using microwave irradiation with a maximum power of 800 W. The optimal conditions identified were a microwave power (MP) of 680 W, irradiation time (IT) of 24 min and substrate concentration (SC) of 75 g/L. Under these optimal conditions, cellulose saccharification (CS), hemicellulose saccharification (HS) and total saccharification (TS) reached 37.8%, 20.2% and 31.8% with increased rates of 30.6%, 43.3% and 30.3% as compared to the straw of raw rice. Therefore, microwave irradiation is an effective pretreatment method and could disrupt the silicified waxed surface, decompose the complex structure of lignin-hemicellulose, and partially remove silicon and lignin thus facilitating the action of cellulases [79].

In the study conducted by Liu et al. [80] on poplar sawdust (80 mesh) it was applied a combined pretreatment using as solvent choline cloride/oxalic acid dihydrate (ChCl/OA) deep eutectic (DES) with pH= 1.31 + microwave treatment and solid to-liquid ratio of 1:20. 80% of total lignin was removed from the samples pretreated only with ChCl/OA after being maintained for 9 hours at 110 °C, while the same results were obtained by applying microwave irradiation for 3 minutes at 800 W [80].

Chen et al. [81] analyzed the impact of microwave-assisted (10 %wt solid loading) pretreatment using a radiation power of 800 W, temperature of 152 °C, and time of 45 s on corn stover, Switchgrass and Miscanthus. After pretreatment, significant amounts of lignin and xylan were identified in the liquid fraction. The lignin content removed from corn stover, Switchgrass and Miscanthus was 79.60%, 72.23% and 65.18%, respectively [81].

3.1.3. Ultrasonic pretreatment

The use of ultrasound is an effective method for separating constituents from LCMs. Ultrasonic treatment is based on the working principle of the acoustic cavity, which is described as spontaneous formation, growth and subsequent collapse of the microsize cavities/bubbles caused by the propagation of ultrasonic waves in the liquid medium. The implosion of these cavities generates high temperatures and pressure gradients locally for microsecond conditions, creating the effect of hot-spot in the liquid [82,83].

Esfahani et al. [84] pretreated sugarcane bagasse (particle size >1, 1-0.5, 0.5-0.18, <0.18 mm) using ultrasound-assisted diluted H_2SO_4 pretreatment (20 kHz, 50, 80, 120 and 200 W; 0, 1, 3 and 5% (v/v) H_2SO_4) for 0, 60, 12 and 180 s, respectively. The most significant impact was recorded when the ultrasound power was 120 W [84].

Yuan et al. [85] have applied an ultrasound-assisted organic solvent pretreatment to delignify poplar wood at 20 kHz, 570 W and 25 °C for 30 min using three organic solvents – 95% ethanol, methanol, and dioxane. Following the application of ultrasound-assisted organic solvents pretreatment, approximately 25.7% of the original lignin was extracted [85].

Sun et al. [86] have pretreated wheat straws using ultrasound-assisted alkali pretreatment at 20 kHz and 100 W with 0.5 M KOH at 35 °C for 2.5 h, and after 35 min of ultrasound irradiation approximately 8.4% of lignin was extracted [86].

3.1.4. Pulsed electric field (PEF) pretreatment

Pulsed electric field (PEF) is a very short non-thermal treatment (from a few microseconds to a few milliseconds) with a pulse amplitude from about 300 V/cm to 20-40 kV/cm. By comparison to other treatments, the damage caused to cell membranes or tissue matrix is lower. In other words, PEF penetrates the biological membrane which temporarily or permanently loses its semi-permeability [87]. The electrical permeability of biological membranes is called electroporation and can be reversible or irreversible [88]. Electrical permeability of different species of Switchgrass and wood chips using PEF can be applied to facilitate the hydrolysis of cellulose to glucose in order to obtain fuels [89].

Almohammed et al. [90] analyzed the impact of pulsed electric field intensity E and duration t_{PEF} on the expression kinetics of dissolved substances in sugar beet tails (SBT). In regards to the intensity and optimal duration of PEF, it was established that E = 450 V/cm and t_{PEF}= 10 ms corresponded to an energy input Q= 1.91 Wh/kg, as the yield of dissolved substances increased from 16.8% to 79.85% by comparisson to untreated SBT. Also, the liquid fraction resulting from the PEF pretreatment was more concentrated (10% vs. 5.2%) and implicitly higher sucrose content was obtained (8.9 °S compared with 4.5 °S in the juice from untreated SBT). Therefore, it was found that by applying the PEF pretreatment it would be achieved an ethanol content of 6.1% v/v, as compared to 2.95% v/v for the untreated SBT [90].

Kumar et al. [89] investigated the impact of PEF on untreated and treated samples of Switchgrass using 1000, 2000 and 5000 pulses of 2.5, 5, 8 and 10 kV/cm with a pulse width of 100 μs and a frequency of 3 Hz, and samples of untreated and treated wood chips (Southern pine), for which they applied 1000 and 2000 pulses of 1 kV/cm and 1000, 2000, and 5000 pulses of 10 kV/cm, the pulse width and frequency being similar. To indicate the impact of PEF on internal diffusion in the tissues of the samples, the absorption of a neutral red dye $C_{15}H_{17}ClN_4$ ($M_W \sim 289$) was studied. In the case of Switchgrass samples, no structural changes were recorded at low field intensities up to 5 kV/cm. Changes in the structure were recorded at field intensities of 2000 and 5000 pulses of 8 kV/cm and 10 kV/cm, respectively. Changes were observed for wood chips treated at 10 kV/cm [89].

3.2. Chemical pretreatments

3.2.1. Acid pretreatment

Compared to the alkali pretreatment which removes more lignin, the acid pretreatment removes more hemicellulose, while cellulose and lignin fractions are less affected [90,92].

Regarding the acid pretreatment of lignocellulosic biomass, mineral acids (HCl, HNO_3, H_2SO_4 and H_3PO_4) and organic acids (e.g. CH_2O_2, $C_2H_4O_2$, $C_3H_6O_2$ and $C_4H_4O_4$) can be used successfully [93]. As their use affects the environment, it is necessary to find pretreatment techniques to optimize yields and reduce costs [94]. Table 2 presents different acids used for pretreatment of LCMs.

Table 2

Different acids used for pretreatment of LCMs

Type of acid	LCM	Process conditions	Reference
HCl	corn stover	1 % (w/w) HCl at 100 - 130 °C for 20 - 40 min	[95]
	grass	1 % (w/w) HCl boiled at 100 °C for 30 min	[96]
HNO_3	corn stover	0.2 - 1 % (w/w) HNO_3 at 120, 140 and 160 °C for 1, 5.5 and 10 min	[97]
	oat hulls	4 % (w/w) HNO_3 at 94 - 96 °C for 4 h	[98]
	sugarcane bagasse	1 % (w/v) HNO_3 autoclaved at 121 °C for 30 min	[99]
H_2SO_4	sugarcane bagasse	2 - 6% (w/w) NaOH at 100 - 128 °C for 0 - 300 min	[100]
	corn stover	0.71 - 1.41% (w/w) H_2SO_4 at 165–195°C for 2.9 – 12.2 min	[101]
	wheat straws	0.75 – 2.25% (v/v) H_2SO_4 at 120, 140 and160 °C for 10, 20 and 30 min	[102]
	rice straws	0.5% (w/v) H_2SO_4 autoclaved at 120 °C (15 lb pressure) for 60 min	[103]
	sugarcane bagasse	0.5 - 3% (w/v) H_2SO_4 at 112.5 - 157.5 °C for 5 - 35 min	[104]
H_3PO_4	corn stover	0.16 – 1.84 % (v/v) H_3PO_4 at 126.36 – 193.63 °C for 1.59 – 18.41 min	[105]
	wheat bran	0.5 - 3% (w/v) H_3PO_4 at 150 - 210 °C for 5 - 20 min	[106]
	sugarcane bagasse	1 % (w/w) H_3PO_4 at 170 and 180 °C for 4 h	[107]
	Eucalyptus benthamii	1% (w/w) H_3PO_4 at 180 - 200 °C for 5 - 15 min	[108]
CH_2O_2	Scots pine sawdust	0.5 – 2.5% (w/v) H_2SO_4 at 100, 120, or 140 °C for 1, 1.5, and 2 h	[109]
		15 – 40% (w/v) CH_2O_2 at 100, 120, or 140 °C for 1, 1.5, and 2 h	
$C_2H_2O_4$	corn cob	0.015 – 0.037 g/g $C_2H_2O_4$ at 120 - 180 °C for 10 - 90 min	[110]
	Yellow poplar sawdust	24 – 139 mM $C_2H_2O_4$ at 160 °C for 2 - 58 min	[111]

3.2.2. Alkali pretreatment

Alkali pretreatment is based on the use of hydroxides such as NaOH, KOH, $Ca(OH)_2$ and NH_4OH for the pretreatment of lignocellulosic biomass, cellulose swelling, partial decrystallization of cellulose [112-115] and partial removal of hemicellulose [115-116]. By applying the alkali pretreatment, lignin can be extracted; this is the basis of the pulping process in order to obtain high quality paper (Kraft process) [91-92]. Most studies were performed on the impact that NaOH has on the complex structure of LCB and it was found that this hydroxide can remove lignin and facilitate the activity of cellulolytic enzymes [117]. Numerous LCMs were subjected to alkali pretreatment methods and these include corn stover, sugarcane bagasse, wheat straws, rice straws, Switchgrass, and sawdust [117-119]. Table 3 presents different hydroxides used for pretreatment of LCMs.

Table 3

Different hydroxides used for pretreatment of LCMs

Type of hydroxide	LCM	Process conditions	Reference
NaOH	corn stover	0.25, 0.5, 1 % (w/v) NaOH at 21 °C for 3, 6, 9 h	[120]
	wheat straws	0.25 - 1.5% (w/v) NaOH was at 121 °C/15 psi for 0.5 - 2.5 h	[121]
	sugarcane bagasse	3% NaOH and thermostated in oven at 121 °C, 60 min	[122]
	Sugarcane tops	3% (w/w) NaOH and thermostated at 121, °C (15 lb pressure), 60 min	[123]
	cotton stalk	1, 2, 3, 4, 5% (w/w) NaOH at 120, 150,180, 200 °C, 45 min	[124]
	spruce sawdust	- 3%, 7%, and 10% (w/w) NaOH at 60 °C for 0.5, 1, and 2 h - 7% NaOH (w/w) at −20 °C and 121 °C for 0.5, 2, and 24 h	[125]
	bamboo	2% NaOH at 120, 140,160, 180 °C, 60 min	[126]
KOH	switchgrass	- 0.5, 1.0, 2.0% KOH at 21°C for 6, 12, 24, 48 h - 0.5, 1.0, 2.0% KOH at 50°C for 6, 12, 24 h - 0.5, 1.0, 2.0% KOH at 121°C for 0.25, 0.5, 1.0 h	[127]
Ca(OH)$_2$	corn stover	0.0 - 0.30 g Ca(OH)$_2$ (g/dry biomass) at 120 °C for 5 h	[128]
	Poplar	0.1 - 0.3 g Ca(OH)$_2$ (g/dry biomass) at 60 – 250 °C for 0.25 - 24 h	[129]
	newspaper	0.05 - 0.3 g Ca(OH)$_2$ (g/dry biomass) at 60 – 150 °C for 1 - 24 h	
NH$_4$OH	corn stover	0.5 - 50.0 wt.% NH$_4$OH at 30 °C for 4 - 12 weeks	[130]
	wheat straws	6.2, 15.4, 24.6 and 30.8% (w/v) NH$_4$OH at 20, 32.2, 50, 67.8 and 80 °C for 6, 14.5, 27, 39.5 and 48 h	[131]

3.2.3. Ozonolysis pretreatment

Ozone (O_3) is considered a strong oxidant and has high solubility in water. It converts to oxygen and has a strong affinity for C-C double bonds in the structure of lignin as opposed to carbohydrates where these bonds are missing. For this reason, ozone can be used for the pretreatment of different agricultural residues and energy crops. The most used ozone pretreatment method is the one made in a fixed bed reactor (with humidity of 20-40%) for 60-180 min, under room conditions [132]. Even if the ozonolysis is exothermic, different pressures and temperatures can be applied [133]. By applying ozone pretreatment, approximately 50% of the lignin present in LCB is depolymerized and removed [134], and the pH of LCB drops to 2-3. By increasing the pH it was observed that the depolymerization of lignin is reduced [133].

Travaini et al. [132] reported that ozone pretreatment of sugarcane bagasse slightly reduced carbohydrates, with cellulose and xylan recovery rates being greater than 92%. In this study the following parameters were varied: 1.37 ± 0.03 - 3.44 ± 0.11% (v/v) O_3, humidity 28 ± 0.11 - 80 ± 0.32% (w/w), and ozonolysis time 45 ± 0.02 - 195 ± 0.02 min. Also, ozonolysis facilitated the enzymatic hydrolysis obtaining the yields of glucose and xylose [132].

In the study by Garcia-Cubero et al. [133] the ozonolysis pretreatment was applied on wheat straws, rye straws, oat straws, barley straws using 2.7% (w/w) O_3 and 40% (w/w) humidity under room conditions [133].

3.2.4. Organosolv pretreatment

Organic solvents are used to extract/remove lignin from LCB before performing enzymatic hydrolysis of the cellulose fraction. In the case of pretreatment with organosolv, single organic solvent or different ratios of organic solvents/water can be used. It was found that in order to increase the solubilization rate of lignin and hemicellulose and their removal it is recommended to use an acid as catalyst to facilitate the enzymatic hydrolysis of the cellulose fraction. The most commonly used organic solvents for the pretreatment of LCMs are ethanol, methanol, acetone and ethylene glycol [135] and the maximum temperature at which they can be used can range up to 200 °C. In some cases it is not necessary to use maximum temperatures, however, depending on the type of LCM lower temperatures can be applied alongside an acidic catalyst [12]. Because the solvent used in the pretreatment of LCM can have inhibitory effects on the enzymatic hydrolysis and fermentation steps, it must be separated and recycled. [14]. Table 4 presents different organosolv and catalysts used for pretreatment of LCMs.

Table 4

Different organosolv and catalysts used for pretreatment of LCMs [68,136]

Type of organosolv	LCM	Process conditions	References
60% Ethanol	corn stover	n-propylamine at 140°C for 40 min	[137]
60% Ethanol	corn stalk	4% NaOH at 110°C for 90 min	[138]
25% Ethanol	wheat straws	1% H_2SO_4 at190°C for 60 min	[139]
50% Ethanol		0.35% H_2SO_4 at 180°C for 40 min	[140]
60% Ethanol		0.29% H_2SO_4 at 190°C for 60 min	[141]
45% Ethanol	rice straws	1% H_2SO_4 at 180°C for 30 min	[142]
65% Ethanol		1.1% H_2SO_4 at 170°C for 60 min	[143]
50% Acetone	barley straws	0.5% H_2SO_4 at 140°C for 20 min	[144]
50% Ethanol		1.6% $FeCl_3$ at 170°C for 60 min	[145]
25% Butanol	sorghum bagasse	0.5% H_2SO_4 at 200°C for 60 min	[146]
50% Ethanol	sweet sorghum	1% H_2SO_4 ar 140°C for 30 min	[147]
50% Ethanol	sugarcane bagasse	1.25% H_2SO_4 ar 175°C for 60 min	[148]
60% Ethanol		0.025% $FeCl_3$ at 160°C for 72h	[149]
70% Glycerol		at 220°C for 120 min	[150]
60% Ethanol	Bamboo	at 160°C 60 min	[151]
56% Glycerol	Eucalyptus wood	at 200°C for 69 min	[152]
25% Ethanol		1% CH_3COOH at 200 °C for 60 min	[153]

3.2.5. Ionic liquids (ILs)

Ionic liquids (ILs) are considered to be environmentally friendly molten salts and are part of a new class of solvents that have high polarity, low melting point, nonvolatility and designability [154-157]. Regarding the pretreatment of lignocellulosic biomass ILs were successfully used as solvents for lignin extraction and crystallinity reduction of carbohydrates [158-159]. ILs offer more attractive features when compared to conventional methods [160]. The physico-chemical properties of the IL, the reaction time and temperature, the ratio between biomass and IL, the type of biomass and the humidity of the sample are the criteria that must be taken into account when selecting the type of IL used for the LCM pretreatment [161]. Compared to conventional methods, ILs have numerous attractive features [160].

For LCB pretreatment, ILs should have the following properties [160,162]:

- ability to dissolve LCB at low temperatures;
- chemical stability;
- low viscosity;
- easy to regenerate and recycle;
- cost-effective and easy to process;- absence of toxicity during enzymatic hydrolysis and microbial fermentation steps.

Numerous studies have shown that higher conversion and/or yields of intermediates can be obtained if metal or acid catalysts are also used alongside ILs [163]. The most representative ILs containing organic cation salts are nitrate [NO3]$^-$, hexafluorophosphate $[PF_6]^-$, alkyl-imidazolium $[R_1R_2IM]^+$, alkylpyridinium $[RPy]^+$, methanesulfonate (mesylate) $[CH_3SO_3]^-$, trifluoromethane sulfonate $[CF_3SO_3]^-$, tetraalkylammonium $[NR_4]^+$, or tetraalkylphosphonium $[PR_4]^+$ and anions, and bis- (trifluoromethanesulfonyl) imide $[Tf_2N]^-$. There are also salts of chloride, iodine and bromide [164]. Table 5 presents different ionic liquids and catalyst used for pretreatment of LCMs.

Table 5

Different ionic liquids (ILs) and catalysts used for pretreatment of LCMs [160]

Type of acid	LCM	Process conditions	Reference
1-butyl-3-methylimidazolium chloride	Corn stalk	HCl at 100 °C for 0.5 h	[165]
		HCl at 100 °C for 5.5 h	
	Rice straws	HCl at 100 °C for 7.5 h	
	Pine wood	HCl at 100 °C for 0.8 h	
	Bagasse	HCl at 66 °C for 1 h	
1-butyl-3-methylimidazolium bromide	Corn stalk	HCl at 100 °C for 1 h	
1-allyl-3-methylimidazolium chloride		HCl at 100 °C for 1.5 h	
1-hexyl-3-methylimidazolium chloride		HCl at 100 °C for 20 h	
1-Ethyl-3-methylimidazolium acetate	Rice straws and cassava pulp	at 25 - 120 °C for 24 h	[166]
1-Ethyl-3-methylimidazolium diethyl phosphate			
1,3-dimethylimidazolium methyl sulfate			
N-methylmorpholine-N-oxide	Spruce and oak	6 %, 90–130 C, 1–3 h	[167]
	Spruce and birch chips	6 %, 130 C, 1–5 h	[168]

3.2.6. Deep eutectic solvents (DES)

Recently, deep eutectic solvents (DES) have attracted more and more attention and are considered to be alternative ILs or in other words are considered to be green solvents that have physico-chemical properties similar to ILs. In most cases, DES contain two or three components that are linked by a hydrogen bond thus resulting an eutectic mixture with a melting point lower than each individual component. [169,170]**.** Usually, below 100 °C DES are in liquid form. Compared to ILs, DES are biodegradable and the production costs are lower [169]. The technology for obtaining DES refers to mixing a quaternary ammonium salt with a metal salt or hydrogen bonding donor (HBD) which can create a complex with the halogen ion of the quaternary ammonium salt [171].

Zhang et al. pretreated 0.3 g of corncob with a DES that was prepared by mixing choline chloride (ChCl) with carboxylic acid (monocarboxylic and dicarboxylic) or polyalcohol at 90 °C for 24 h [172]. Xu et al. pretreated corn with an acid DES consisting of choline chloride: formic acid (ChCl: CH_2O_2) and obtained noteworthy results in terms of removal of hemicellulose and lignin [173]. Also, Pan et al. [174] pretreated 10 g of rice straw with 200 g ChCl/urea and transferred the mixture to 500 ml Erlenmeyer flasks. Then, the contents were stirred and maintained at 110 °C and 130 °C for 4 h, 6 h and 8 h, respectively [174]. Jablonský et al. [175] pretreated wheat straw with six types of DES using different ratios of choline chloride with urea, malic, lactic, malonic, lactic, and oxalic acid. 2.5 g of wheat straw were pretreated with individual DES at a ratio of 1:20 (w/w) for 24 hours at 60 °C; for choline chloride and urea and choline chloride and malic acid the temperature was 80 °C [175].

4. Advantages and disadvantages of physical and chemical pretreatments

Regarding the technological process of bioethanol production from LCM, selection of the pretreatment type specific to each LCM is very important because this step has a great impact on all subsequent steps (hydrolysis and fermentation) [176]. Therefore, the choice of pretreatment should be made carefully in the process of obtaining bioethanol because the pretreatment also affects the cost of the next steps of operation and refers to the determination of compounds that cause inhibition of fermentation, enzyme hydrolysis rates and enzyme dosages alongside other factors that may influence the fermentation process. Table 6 shows the main advantages and disadvantages of the most common pretreatment technologies used for the conversion of LCB to bioethanol [177].

5. Conclusion

The growing need for energy worldwide and environmental pollution must lead us to focus on the exploitation of lignocellulosic biomass, which is a renewable source that is widely available and relatively inexpensive. In order to convert LCMs to bioethanol, their complex structure must first be fractionated as much as possible. This can be done only by correctly choosing from the various pretreatment technologies available, which include biological, mechanical, chemical and various other combined methods.

Table 6
Advantages and disadvantages of the most common pretreatment technologies used for the conversion of LCB to bioethanol [177,178]

Pretreatment	Increases accessible surface area	Cellulose decrystallization	Hemicellulose solubilization	Lignin removal	Lignin structure modification	Production of toxic compounds
Mechanical	+++	+++	0	0	0	0
Irradiation	+++	+++	+	+++	+++	+
Acid	+++	0	+++	++	+++	+++
Alkali	+++	+++	++/+++	+++	+++	+
Ozonolysis	++	++	++/+++	+++	++	+
Organosolv	++		+++	++/+++	++	++/+
Ionic liquids	++	+++	+++	++/+++	++	++/+

(+++) high effect; (++) moderate effect; (+) low effect; (0) no effect

Physical pretreatment methods, and especially mechanical ones, reduce the crystallinity and particle size and cause an increased contact surface with the pretreatment agent. However, this process generates high energy consumption and therefore high costs.

In regards to the application of chemical pretreatment methods, the use of chemicals such as acids, alkalis, ozone or organic solvents can effectively remove lignin, thus facilitating the enzymatic hydrolysis of cellulose.

We cannot name a method that is the best choice and can be applied among all types of lignocellulosic biomass. The choice of pretreatment method depends for the most part on the type of LCB and therefore each pretreatment method has its own effects on the cellulose, hemicellulose and lignin fractions.

6. Reference

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