



Review Intensification of Bioethanol Production from Different Lignocellulosic Biomasses, Induced by Various Pretreatment Methods: An Updated Review

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Abstract: While world energy demand has certainly decreased with the beginning of the COVID-19 pandemic in 2020, the need has been significantly on the rise since 2021, all as the world's fossil fuel resources are depleting; it is widely accepted that these resources emit greenhouse gases (GHG), which are the leading cause for the climate crisis. The main contributors to global warming are manufacturing, energy, and agriculture. The agricultural sector is composed of diversified and potential mobilizable sources of waste which can become an attractive alternative to fossil fuels for energy production, and thus sequester and use carbon. Therefore, a paradigm shift towards more sustainable energy alternatives, efficient waste management, and new technologies is necessary. One good solution is the energetic valorization of lignocellulosic biomass (LCB) which can also originate from agricultural wastes. The biomass consists of cellulose, hemicellulose, and lignin, which are sources of fermentable sugars that can be used for bioethanol production. However, the recovery of sugars requires the pretreatment of LCB before enzymatic hydrolysis, due to its inaccessible molecular structure. Different pretreatment technologies, including acid and alkaline pretreatments for selected biomasses (such as hemp, rice straw, corn straw, sugarcane bagasse, and wheat straw) are discussed and compared. Therefore, this review highlights the potential of agricultural waste as a renewable resource for energy production.

Keywords: biofuels; energy conversion; delignification

1. Introduction

Climate change is driven mainly by the burning of fossil fuels, which results in GHG emissions into the atmosphere; it has been recorded that 89% of total carbon dioxide, a greenhouse gas, that was emitted into the atmosphere in 2018 originates from fossil fuel sources [1,2]. However, following the menace of the COVID-19 pandemic, these GHG emissions have dropped by 4.6% in 2020 due to the hindered economic activity. Nevertheless, the emissions rose again significantly by 6.4% in 2021, with the manufacturing and energy sectors contributing the more substantially [3]. British Petroleum reported that fossil energy demand has declined in 2020 (Figure 1), but also highlighted that the demand for renewable energy has noticeably increased [4].

Another important contributor to the emission of GHGs is the agricultural sector, as it has sought to achieve two goals: increase crop yields and maximize economic profit. To reach those outcomes, more modern practices were developed, including monoculture, rigorous tillage, irrigation, and chemical pest control. However, all these practices require



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). fossil fuels for their application, in addition to the fossil fuels utilized for transportation and machinery [5–9], implying that GHG is released into the atmosphere at every stage, from land to final product. For instance, farming releases considerable amounts of methane and nitrous oxide, which respectively originate from livestock during the digestion of foods in the animals' digestive tract and mineral nitrogen fertilizers [10].



ANNUAL CHANGE IN ENERGY DEMAND (2020; %)

Data collected from as early as 1998 about the United States' (U.S.) use of fossil fuels indicates that U.S. agriculture alone was responsible for 116 out of the total 1596 million metric tons of carbon equivalent (MMTCE) of U.S. emissions [11]. Moreover, the Food and Agriculture Organization (FAO) has reported that world livestock emit 7.1 Gigatons of CO₂ eq yearly, corresponding to 14.5% of GHG emissions, with feed production and cattle's digestion being the two main sources. What is left of the total emissions by the agricultural sector is drawn back to transportation, food processing, and manure storage [12]. On a larger scale, the global agriculture sector accounted for 17% of the total world GHG emissions in 2018 [13], and the United States emitted 11% GHG in 2020; it was also recorded that 422,843 kT CO₂ eq were emitted by the Member States of the European Union and the United Kingdom [14,15].

Furthermore, this sector is also responsible for significant waste generation, which is consequently hazardous to food safety, the environment, and global health [16]. One of the current priority of world leaders is to provide sufficient food and energy for the increasing population, all while reducing fossil fuel and solid wastes [17]. Thus, as agriculture contributes to climate change, the latter harms the agricultural sector through changes in precipitation patterns and negative effects on crop yield, for example [18–20]. In addition, many agricultural practices excessively exploit the earth's natural resources, further negatively altering the environment [21] (Figure 2).

Therefore, in light of the multiple environmental issues that the planet is facing today, there has been a rising awareness about the repercussions of these issues and an increasing demand for a shift toward more sustainable strategies and practices, as well as for more sustainable energy alternatives. The latter include solar energy, hydropower, geothermal power, wind energy, and biomass [23]. The alternatives are presented as more natural solutions, and they all allow for the reduction of GHG emissions. However, the additional advantage of biomass is that it can stem from wastes and can be transformed into various forms of products, such as heat when burned or biofuel when processed. Planting crops specifically for biofuel production, in itself, induces environmental stress, as there will be

Figure 1. Predicted vs. actual annual change in energy demand (2020; %).

no variation in planting [24,25]. However, since biomass can also originate from wastes, this valorization becomes an asset in reducing wastes left in the environment. There exist different types of biomasses for the production of biofuels; these biomasses can be starch-based, sugar-based, or lignocellulosic, meaning they are composed of cellulose, hemicellulose, and lignin. As for lignocellulosic biomass, they are of three types, shown in Figure 3 along with some examples of each [26].



Figure 2. The effect of climate change and agriculture on each other [22].



Figure 3. The three types of lignocellulosic biomass with some examples of each.

The literature describes distinct types of promising biomasses tested for bioethanol production, and whose chemical composition is described in Table 1. Overall, LCB are promising raw materials because they are abundant and economic. For instance, wheat is considered one of the most ancient and most important crops worldwide, with a world production of 779,243 (1000 MT) in 2021 [27,28]. Moreover, the hemp market has risen in popularity, even if about 50% of the world's hemp fiber supply is produced in China, which planted 667 km² of hemp in 2019 [29]. Additionally, the U.S. grew approximately 220 km² of industrial hemp in the open in 2021, and the E.U. cultivated approximately 350 km² in 2019 [30,31]. Furthermore, corn is one of the most distributed crops worldwide, in addition to being the U.S.'s leading crop, having planted 97,000 km² of land with

corn in 2019 [32,33]. Rice, on the other hand, is a primary necessity for over half of the world's population. The U.S. Department of Agriculture (USDA) estimates World Rice Production to reach 514.76 million metric tons in 2022–2023, which represents a 0.23% increase in worldwide rice production compared to 2021–2022 [34,35]. Finally, sugarcane is also classified as one of the world's most important crops, especially that 267,743 km² were harvested worldwide in 2016. Moreover, Brazil ranked first worldwide in sugarcane production volume, with a volume equivalent to 41% of world production in 2017 [36]. The abundance and mass production of these crops implies a significant generation of agricultural wastes. The latter is also inexpensive and is characterized with its naturally complex structure, so its valorization for energy production can be presented as promising and as an attractive alternative.

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Biomass	Cellulose Hemicellulose		Lignin	References
Hemp	40.1–75.6	10.1–14.2	10.3–14.6	[6,37–40]
Rice straw	28.0-34.7	20.0–25.2	17.0–19.0	[26,41]
Corn stalks	31.0–39.0	16.5–35.0	16.6–25.4	[26,42–44]
Sugarcane bagasse	25.0-45.0	28.0-32.0	15.0-21.0	[26,45]
Wheat straw	31.0–39.0	23.0-43.0	12.0-22.0	[26,46,47]

 Table 1. Chemical composition of promising lignocellulosic biomasses.

It is worth noting that the production of biofuels from biomasses has already been taken to an industrial level, with several facilities built around the world: 86 million tons of bioethanol were produced in 2018, with the main producers divided as shown in Figure 4. Additionally, the U.S. Energy Information Administration (EIA) reported that 4835 trillion British thermal units (TBTu) were provided by biomass in 2021, and that is equivalent to 1.416×10^{16} kWh [48].



Bioethanol production (2018; %)

Figure 4. Bioethanol production (%) by the six main producers: the U.S., Brazil, Europe, China, Canada, and India (2018).

However, some of these facilities are operational, while others are either ceased, planned, still under construction, or empty. The main reasons for the lack of operational facilities are due to financial difficulties or lack of adequate technology [49]. In fact, it is important to know that the structure and organization of the three polymers constituting lignocellulosic biomass depend on the types of biomasses, which also have a varying composition of each polymer. Furthermore, the multi-scale structure of those fibers, as well as the presence of lignin, is recalcitrant to enzymatic hydrolysis, which is applied to allow the release of fermentable sugars that will, in their turn, yield bioethanol following fermentation [50–52]. Therefore, this biomass requires a pretreatment to enhance the accession.

sibility of the enzymes to the fibers, hence increasing the bioconversion and fermentation yields. The various other kinds and varieties of lignocellulosic biomass, as well as the different pretreatment parameters to be considered, led to the suggestion of numerous pretreatment techniques for different types of available lignocellulosic biomasses, and were presented with the overall procedure in Figure 5. Choosing the appropriate pretreatment technique and conditions plays a role in the outcomes of subsequent processes. Therefore, several factors need to be considered, such as energy cost, eco-friendliness, duration of pretreatment, and conservation of the fermentable sugars. In general, the efficiency of pretreatment for biofuel production is often defined by the lignin, cellulose, and hemicellulose contents after pretreatment, reducing sugar yield/concentration obtained following enzymatic hydrolysis, and biofuel yield/concentration obtained following fermentation.



Figure 5. General overview of bioethanol production from lignocellulosic biomass.

The purpose of this review is primarily to compare the recent applications and efficiencies of several pretreatment techniques applied to enhance the hydrolysis, and potentially the fermentation, of the most promising lignocellulosic biomasses: hemp biomass, corn stover, rice straw, wheat straw, and sugarcane bagasse.

2. Pretreatment of Hemp Biomass

Raw hemp biomass consists of 35–51% cellulose (dry basis, db), 13–28% hemicellulose (db), and 12–22% lignin (db), a compositional difference that can be explained by the presence of various hemp cultivars [53–55] and the focus on different parts of the biomass (stems, woody core, hurds). Generally, the raw biomass is subject to drying to reduce its moisture content, as the latter critically affects the pretreatment's conversion proficiency [56]. Furthermore, hemp biomass is subject to particle size reduction (milling, grinding, sieving, etc.), before pretreatment, to increase the surface area accessibility, hence allowing better enzyme digestibility of the biomass's constituents [57,58].

Improvement of enzyme digestibility is the key purpose for pretreatment, which can be physical, chemical, biological, or a combination of two or more. Chemical pretreatment, more specifically alkaline pretreatment, is the most commonly used for hemp biomass [59–64], as it has been proven most effective for de-lignification [65], which will in its turn improve enzymatic hydrolysis by diminishing the biomass's recalcitrance. Sodium hydroxide (NaOH)-based pretreatments were performed using 1–3% NaOH, temperatures greater than 90 °C, and for durations of 0.5–5 h [59,60]. High temperatures are employed because they play a role in lignin deformation, enhancing enzymatic hydrolysis [66]. Other experiments that have used NaOH have also utilized sulfuric acid (H₂SO₄) and Liquid Hot Water (LHW) [62], acetic acid (HOAc) [63], or sodium chlorite solution (NaClO₂) [64]. However, NaOH-based pretreatment was more effective in biomass treatment than H₂SO₄- based processes or LHW [62]; it was also performed alongside NaClO₂-based pretreatment to finally obtain differently treated samples of varying cellulose, hemicellulose, and lignin contents. The latter yielded holocellulose hemp hurd (HHH, 32.73% hemicellulose), lignin-containing hemp hurds (LHH, 17.99% lignin), and α -cellulose hemp hurds (AHH, 78.03% cellulose). Moreover, NaOH-treated samples were subject to two-volume (II-VW) washing, then merged with HOAc-treated samples to eliminate NaOH-soluble lignin [63]. The outcomes of these pretreatment experiments were summarized in Table 2.

Additionally, aqueous ammonia soaking was conducted using 10% NH₄OH for a process held at 70 °C for 22 h; it is important to note that time and temperature pairs (high temperature-short duration or low temperature-long duration) were described for acidic pretreatments [66], but appear also to be applied to alkaline pretreatments.

On another note, a combined biological-chemical pretreatment was achieved using white-rot fungi and alkaline oxidative pretreatment (3% NaOH and 3% H₂O₂) [67]. The combined pretreatment was performed over 24 h at 40 °C, and four other fungi were tested, of which *Pletorus eryngii* exhibited the best performance.

Chemical and combined pretreatment have notably resulted in a significant decrease in lignin content, from 12–22% to 7–18%. In contrast, the content of cellulose, the polymer of interest for hydrolysis and subsequent fermentation, has noticeably increased from 35–51% to reach 62–78%, which could be caused by the removal of lignin that was blocking the cellulose before pretreatment [68].

Following pretreatment, Simultaneous Saccharification and Fermentation (SSF) was accomplished [59,60,62] with optimization by Response Surface Methodology (RSM) [60] or by individually-elaborated experimental conditions [59]. The latter consisted of four scenarios in which the composition of the fermentation medium (cellulase, hemicellulase, and presence/absence of Tween 80) was different for the four SSF trials. The fourth case (30 FPU/g cellulase, 140 FXU/g hemicellulase, and milling (size = 0.22 mm)) proved to be most efficient. Moreover, regular enzymatic hydrolysis was also performed following pretreatment [62,64,68].

Finally, ethanol content produced varies remarkably following chemical pretreatment and saccharification. For instance, 6.5 g/L produced after 96 h of fermentation [60] as opposed to 76.92 g/L also produced after 96 h of fermentation [59], despite both studies undergoing an optimization process. The lower ethanol concentration could result from of the increased lignin content following chemical pretreatment, which consequently affects the efficiency of SSF. On the other hand, the second optimized process using the four different cases allowed the comprehension between ethanol concentration and solid loading, which exhibited a significantly negative quadratic correlation. Therefore, fermentation was repeated at the focus point of the quadratic model defined for the fourth scenario (30 FPU/g cellulase, 140 FXU/g hemicellulase, and milling (size = 0.22 mm)), which resulted in 76.92 g/L of ethanol. In addition, 20.1 g/L of ethanol was obtained after 72 h of fermentation [63], a concentration that can be attributed to the efficiency of the pretreatment in removing lignin (from 14.56% to 9.21%), which allowed for an effective hydrolysis.

To conclude, NaOH remains the most effective chemical agent in hemp biomass pretreatment as it has confirmed its efficiency in de-lignification, hence the reduction of recalcitrance to enzymatic hydrolysis. Moreover, these studies confirm that solid loading also plays an important role in final ethanol concentration [59]. Nevertheless, more information should be gathered about the efficiency of other non NaOH-based pretreatments, or treatments based on the application of NaOH and other agents, in relation to bioethanol production.

Raw Material	Biomass Preparation	Pretreatment	Composition (Treated; % db)	Saccharification	Reducing Sugars	Fermentation	Bioethanol	References
Tygra hemp biomass (<u>Cellulose</u> : 50.82% <u>Hemicellulose</u> : 27.79% <u>Lignin</u> : 14.68%)	 Crushing (20–40 mm) Drying (24 h, 50–55 °C) Milling (size = 2 mm) 	<u>Chemical:</u> 2% NaOH, 90 °C, 5 h	<u>Cellulose</u> : 62.7% <u>Hemicellulose</u> : 20.16%, <u>Lignin:</u> 15.12%	 Celluclast 1.5 L + enzyme mixtures Glucosidase/xylanase supplementation Optimization of SSF using RSM Optimal: Flashzyme Plus 200/ Celluclast 1.5 L (70/30%), substrate 5%, 37 °C, pH 4.8, 120 h 	<u>Total RS:</u> 2311 mg/g	S. cerevisiae 37°C, 900 rpm, pH 4.8, 96 h 1 N NaOH or 1 N HCl,	6.5 g/L (13 g/ 100 g of biomass)	[60]
Hemp stems (Cellulose: 40.66% Hemicellulose: 13.25% Lignin: 15.74%)	Drying (49 °C, 72 h) Grinding (< 2 mm)	 <u>Chemical:</u> 1% NaOH, solid-liquid ratio 1:10 Uninterrupted air blast (30 min, until 170 °C reached) Vacuum filtration Washing until neutral pH Over-night drying (49 °C) 	<u>Cellulose:</u> 77.54 % <u>Hemicellulose</u> : 8.72% <u>Lignin:</u> 11.05 %	 Optimization of SSF using <u>4 cases:</u> <u>Optimal:</u> cutting (size < 0.2 mm), cellulase 30 FPU/g, Hemicellulase 140 FXU/g, 96 h 1 mL of yeast culture, 37 °C, 140 rpm 	N.D. ¹	S. cerevisiae (1 mL) SSF (focus point of quadratic equation): solid loading 31%, 37 °C, 96 h, 140 rpm	76.92 g/L	[59]
Industrial hemp biomass (<u>Cellulose</u> : 40% <u>Hemicellulose</u> : 18% <u>Lignin:</u> 16%)	 Grinding Pulverization (size < 2 mm) 	Chemical:NaOH (0.05 M, pH 12.71, solid-liquid ratio 1/10, 190 °C, 40 min) or HOAc (1 M, pH 2.36) - Vacuum filtration - Two-volume water (II-VW) washing - Drying (49 °C) - Merging of NaOH and HOAc filtrates (20 min) - Vacuum filtration	<u>Cellulose:</u> 73.61% <u>Hemicellulose</u> : 12.2% Lignin: 7.51%	Enzymatic hydrolysis: 2.5–10% solid loading, pH 4.8, 100 μL cellulase/g biomass, 50 μL hemicellulase/g biomass, 160 rpm, 49 °C, 72 h	Focus point (II-VW): <u>Glucose</u> : 43.88 g/L <u>Xylose</u> : 12.13 g/L	N.P. ²	N.D. ¹	[63]
Hemp woody core (<u>Cellulose</u> : 37.3% <u>Hemicellulose</u> : 19.79% <u>Lignin:</u> 12.35%)	Preculture (<i>P. eryngii</i> , PDA, 28 °C, 7 days) Cutting (400–800 μm) Air-drying	Biological: - Substrate inoculation - Incubation (28 °C, 21 days) - Drying (50 °C, 3 days) - Chemical: 3% NaOH, 3% H ₂ O ₂ - Bio-chem; 40 °C, 24 h	N.D.	Enzymatic hydrolysis: cellulase: 30 FPU/g, citric acid buffer (pH 4.8), 0.01% sodium azide, 50 °C, 48 h	<u>RS (Bio-chem):</u> 372 mg/g	N.P.	N.D.	[67]

Table 2. Summary of the recent experiments done for pretreatment of hemp biomass.

Table 2. Cont.

Raw Material	Biomass Preparation	Pretreatment	Composition (Treated; % db)	Saccharification	Reducing Sugars	Fermentation	Bioethanol	References
Helena hemp stems		Three treatments were done: acidic,	After alkaline PT					
(<u>Cellulose</u> : 40.13%	Oven-drying (49 °C, 72 h)	alkaline, and LHW <u>Chemical:</u> 1% NaOH, solid-liquid ratio 1:10, 170 °C, 30 min	<u>Cellulose:</u> 73.9%	Enzymatic hydrolysis: Cellic [®] CTec3 (30 FPU/g), NS22244	<u>Glucose:</u> 40.08 g/L	Incubation 1 g Ethanol Red [®] yeast, 38 °C, 160 rpm, 25 min.	20.1 g/L	[62]
12.53%	(< 2 mm)	 Vaccum filtration Washing Over-night drying (49 °C) 	Vaccum filtration $\frac{140}{7.59\%}$ 50°	(140 FXU/g), solid loading 5%, 50 °C, 72 h, 140 rpm		SSE: 37 °C		
Lignin: 14.56%)			Lignin: 9.21%			140 rpm		
Hemp hurd		<u>Chemical</u> : 1.4% acidified NaClO ₂ (70 °C 5 b) and 4% NaOH (70 °C	HHH:					
(<u>Cellulose</u> : 45.66%	Decortication (aqueous decort. 50°	$(70^{\circ} \text{ C}, 51)$ and 4% NaO11 (70^{\circ} \text{ C}, 2 \text{ h}, $\times 2)$	32.73%					
Hemicellulose: 24.57%	Injection during incubation $(34\% H_2O_2)$ Alkaline agent (30 g,	 Waste removal (etOH-deionized water ratio 1:1, 5×) Rinsing (Milli-Q water until 	LHH: Lignin: 17.99%	N.P. ²	N.D. ¹	N.P.	N.D.	[64]
Lignin: 21.67%)	incubation 5 min) Rinsing + milling (2 mm)	neutral pH) - Vacuum filtration - Oven-drying (70 °C, 24 h)	<u>AHH:</u> <u>Cellulose:</u> 78.03%					

¹ N.D. = Not determined, ² N.P. = Not performed.

3. Pretreatment of Corn Stover

Raw corn stover is composed of 34–39% cellulose (db), 21–25% hemicellulose (db), and 13–21% lignin (db), a variability also drawn back to the existence of several varieties [69]. Corn stover is most often dried before pretreatment to reduce the moisture content and undergoes particle size reduction.

Chemical pretreatment is also highly used for corn stover. Still, unlike hemp biomass, the treatments of corn stover made use of lime $(Ca(OH)_2)$ [70,71], quicklime (CaO) [72], Oxalic acid (OA) [72], and sodium hydroxide (NaOH) [73]. Lime pretreatment was performed alone and optimized using Response Surface Methodology (RSM), with optimal conditions (121 °C, 1 h, 0.1 g/g lime loading) [70], and was likewise performed (0.1 g/g lime loading) and followed by a thermal autoclave treatment of optimal conditions (121 °C, 35% solid loading, 45 min) [71]. Moreover, OA pretreatment was achieved using 2% oxalic acid (1:20 w/v) and was assisted with either autoclave or ultrasonic treatment. Between the two, autoclave-assisted OA treatment was more efficient [74], and was therefore optimized using RSM, which revealed that the optimal conditions were 140 °C, 60 min, 3% oxalic acid, and a solid-liquid ratio of 1:30. Finally, NaOH pretreatment was performed using 1% NaOH in a process maintained at 60 °C for 48 h [73]. Overall, these chemical pretreatments increased cellulose content from 34–39% to 38–57%, simultaneously decreasing lignin content from 13–21% to 10–15%.

Saccharification was performed through SSF [70,73] or regular enzymatic hydrolysis [72,73,75]. Regarding SSF, the latter lasted 96 h [70] or 144–168 h [73]. The 96-h SSF resulted in a glucose concentration >15 g/L, while the glucose quantified by HPLC in the second SSF process amounted to 24.5 g. On the other hand, sole enzymatic hydrolysis resulted in 7.49 g/L of glucose [73], which was considerably lower than 20.41 g/L [72] and 81.2 g/L [71]; this is a possible indicator that, while autoclave-assisted OA pretreatment de-lignified the corn stover biomass more efficiently than ultrasonic-assisted OA pretreatment, oxalic acid is not the most convenient chemical agent for corn stover pretreatment in comparison to lime and quicklime. The results of the pretreatments were summarized in Table 3.

Furthermore, the fermentation step of SSF [70] was performed for 1 h at 121 °C, with the use of *S. cerevisiae* only, resulting in an ethanol concentration of 28.73 g/L; this concentration is greater than the one obtained during fermentation using a mixed culture of S. cerevisiae and Candida cantarelli as inoculum, equal to 18.56 g/L [73]. The slight difference in ethanol concentration could result from the initial glucose contents obtained after hydrolysis. Additionally, while mixed yeast cultures allow for the fermentation of all available sugars in the medium, it cannot be neglected that parameters such as initial inoculum size, pH, or other environmental factors influence the outcome [75], even if the process was optimized. Moreover, batch fermentations were conducted [72,74] for 30 h and 72 h, respectively. The interesting difference is the use of S. cerevisiae only [74], as opposed to the testing of two microorganisms, S. cerevisiae and Wickerhamomyces sp. in two separate fermentations [72]. An ethanol concentration of 3.6 g/L was yielded at the end of the fermentation where S. cerevisiae alone was used, whereas similar quantities (3.10 g/L and 2.80 g/L) were obtained in less than 5 h of fermentation by S. cerevisiae and Wickerhamomyces sp., respectively; this difference results from the significant variation in yielded fermentable sugars following enzymatic hydrolysis, but also can be related to Wickerhamomyces' reported ability to ferment pentoses [76].

These studies suggest that corn stover is a valuable resource for bioethanol production, but also confirm that lime is the most efficient chemical agent for corn stover pretreatment. Additionally, including hexose-fermenting and pentose-fermenting microorganisms within the same fermentation could enhance the bioethanol concentration produced, as both types of microorganisms would be fermenting the preferential sugar.

Raw Materials	Biomass Preparation	Pretreatment	Composition (Treated; % db)	Saccharification	Reducing Sugars	Fermentation	Bioethanol	References
Corn stover feedstock (Cellulose: 37.57% <u>Hemicellulose</u> : 24.37% <u>Lignin:</u> 17.99%)	 Milling (< 8 mm) Air drying Milling (0.5 mm) 	<u>Chemical:</u> liquid-solid ratio 12 g/g, lime (0.1–0.4 g/g _{biomass}) <u>Optimization by RSM</u> (Optimal: 121 °C, 1 h, lime loading 0.1 g/g) - Filtration - Washing until neutral pH	<u>Cellulose:</u> 45% <u>Hemicellulose:</u> 20.8% Lignin: 14.7%	Enzymatic hydrolysis: Celluclast 1.5 L (15 FPU/g), β -glucosidase, 35 °C, pH 5, citric acid buffer 0.05 N, 150 rpm, liquid-solid ratio 20 g/g, β -glucosidase-to- cellulase ratio 5 IU/FPU, 120 rpm, 96 h	<u>Glucose</u> : > 15 g/L (24 h)	<i>S. cerevisiae</i> preculture (32 °C, 24 h, 200 rpm) <u>SSF</u> Centrifugation Filtration	28.73 g/L	[70]
Corn stover								
(<u>Cellulose</u> : 38.5% <u>Hemicellulose</u> : 21.6% <u>Lignin:</u> 20.4%)	Pelletization	<u>Chemical</u> : 0.1 g/g Ca(OH) ₂ <u>Thermal</u> : autoclave, 121 °C, 35% solid loading	<u>Cellulose:</u> 36.7% <u>Hemicellulose:</u> 14.3%	Enzymatic hydrolysis: Cellic [®] CTec 2 cellulase, 20% solid loading, 50 °C, pH 4.8, 250 rpm	<u>Glucose</u> : 81.2 g/L Xylose: 31.3 g/L	<i>S. cerevisiae</i> preculture (30 °C, 150 rpm) <u>Fermentation</u> : 30 °C, 150 rpm	70.6 g/L	[71]
Corn stover (<u>Cellulose</u> : 35.7% <u>Hemicellulose</u> : 21.5% <u>Lignin:</u> 20.1%)	 Chopping, washing Oven-drying (60 °C, 72 h) Grinding (size < 250 μm) 	Two treatments: autoclave-assisted (AA) and ultrasonic-assisted (UA) <u>Chemical</u> (AA): 2% oxalic acid (1:20 w/v), autoclave (120 °C, 60 min, 310 kPa) Vacuum filtration Washing with hot water until neutral pH Oven-drying (50 °C, 12 h) Optimization by RSM (Optimal conditions: 140 °C, 60 min, 3% oxalic acid. S-L ratio 1:30)	<u>After AA</u> : <u>Cellulose</u> : 56.6% <u>Hemicellulose</u> : 12.7% Lignin: 10.9%	Enzymatic hydrolysis: Cellulase (<i>Novozymes</i>), 20 FPU/g, loading 0.4 g, substrate-buffer ratio 1:25, sodium acetate (0.05 M, pH 5), 50 °C, 100 rpm, 96 h	<u>Glucose</u> : 7.49 g/L	Preculture of S. cerevisiae (YPD, 30 °C, 150 rpm, 36 h) <u>Batch fermentation</u> : 5% yeast inoculum (v/v), 30 °C, 72 h	3.6 g/L	[74]

Table 3. Summary of recent experiments done for pretreatment corn stover.

4. Pretreatment of Rice Straw

The composition of raw rice straw ranges between 24–41% for cellulose (db), 10–24% for hemicellulose (db), and 15–25% for lignin (db), and such variability is due to the different varieties available [77]. Rice straw is subject to drying and particle size reduction before pretreatment.

In chemical pretreatment, the techniques employed for rice straw structural modification involve the use of NaOH [78,79], KOH [79], ionic liquids [80,81], nonionic surfactants [80], and N-methylmorpholine N-oxide (NMMO) and phosphoric acid [82]. To begin, 5% NaOH and 5% KOH were both applied using traditional soaking (solid-liquid ratio 1:10) and spraying (solid-liquid ratio 1:5). Following this first chemical treatment, the samples were subjected to a second mechanical treatment known as centrifugal milling, through which the samples' particle size was further reduced. The 5% NaOH soaking pretreatment was more promising in terms of de-lignification, as it efficiently decreased lignin content from 24.7% to 8.37%. Moreover, ionic liquid-based pretreatment was first achieved by a biological-chemical approach, by combining an ionic liquid ([AMIM]Cl) or a nonionic surfactant (Triton X-100), to Laccase [80]. The latter is an enzyme which catalyzes oxidative reactions and is capable of breaking down lignin [83], therefore the trials have coupled either [AMIM]Cl or Triton X-100 with Laccase, just as the enzyme was tested alone. The treatment combining Laccase and Triton X-100 de-lignified the samples successfully, decreasing lignin content from 15.79% to 10.77% after a 24-h pretreatment. [AMIM]Cl is often used for the dissolution of cellulose and its restoration [84]. At the same time, Triton X-100 is a detergent frequently used to remove all cellular components of different tissues [85], an effect that showed greater benefit when combined with a de–lignifying enzyme. However, the dissolution of cellulose is a characteristic of chemical agents used for rice straw pretreatment, such as [EMIM]Ac [81] and NMMO [82], to obtain cellulose and regenerate it by addition of water, ethanol, or acetone [86]. The process involving [EMIM]Ac was optimized using RSM (optimal conditions: 5% solid loading, 128.4 °C, 71.83 min), while the NMMO-based pretreatment was compared to phosphoric acid-based pretreatment and proved to be more effective in terms of de-lignification (from 16.7% to 13.2%) [82] (The outcomes are summarized in Table 4).

Moreover, SSF was carried out following the NMMO-based treatment and was maintained at 45 °C for the hydrolysis step. At the end of the saccharification, more than 100 g/L of glucose was obtained, which indicates that NMMO efficiently dissolved cellulose which was then successfully regenerated and made available for hydrolysis [82]. Soaked NaOH pretreatment allowed the production of 0.52–0.63 g_{glucose}/g_{biomass} at the end of enzymatic hydrolysis (72 h) [79], which is almost equivalent to the glucose concentration obtained following hydrolysis of [EMIM]Ac-treated samples (0.573 g_{glucose}/g; 72 h) [81].

Furthermore, a variety of microorganisms were employed for the fermentation of rice straw: *M. indicus* [82], *S. cerevisiae* [81], and *P. stipitis* [78]. A 5 g/L inoculum of *M. indicus* was used for the fermentation and yielded 44.2 g/L of ethanol at the end of the 72-h SSF process, which was remarkably greater than 5.9 g/L resulting from *S. cerevisiae* fermentation; it was greater than 3.32 g/L following 48 h of fermentation by *P. stipitis*. Considering the significant glucose concentration obtained following NMMO pretreatment, it is not surprising that such an ethanol yield was obtained, as opposed to lower sugar concentrations available in the medium for fermentation by *S. cerevisiae* and *P. stipitis*. Therefore, it can be concluded that NMMO is the most efficient chemical agent for the pretreatment of rice straw.

Fortunately, NMMO is also an eco-friendly agent [87] that has allowed for the dissolution of cellulose, for it to be recovered and efficiently hydrolyzed. Furthermore, a quick overview of the potential of non-conventional yeasts (*P. stipitis*) for fermentation of pretreated biomass was given, encouraging their use for further applications.

Raw Materials	Biomass Preparation	Pretreatment	Composition (Treated; %db)	Saccharification	Reducing Sugars	Fermentation	Bioethanol	References
Rice straw		Chemical: NaOH and KOH (5%), 3 h,	Soaking, 5% NaOH					
(<u>Cellulose</u> : 24.1%	- Grinding	25 °C - Soaking (S-L ratio 1:10) and	<u>Cellulose</u> : 43.54%	Enzymatic hydrolysis: Cellic [®] CTec 2 (<i>Novozymes</i>)	<u>Glucose:</u>			
<u>Hemicellulose</u> : 10.9%	- Sieving	- Oven-drying (60 °C)	Hemicellulose: 8.62%	sodium acetate buffer, pH 5, 5% sodium azide, 50 °C,	0.52–0.63 g/g	N.P. ²	N.D. ¹	[79]
Lignin: 24.7%)		<u>Mechanical</u> : Centrifugal millng (size = 0.25 mm), 25 °C, 2 min	Lignin 8.37%	72 h, 200 rpm				
Rice straw		Three pretreatments: Laccase only. Laccase	Laccase + tv					
(<u>Cellulose</u> : 31.73%	- Drying (25 °C)	+ [AMIM]Cl, or Laccase + TritonX-100 Chemical Laccase + TX: Triton X-100 (0.5 g/L), 0.1 M citrate buffer, pH 4.5,	<u>Cellulose</u> : 40.83%	Enzymatic hydrolysis: beta-glucosidase (40 CBU/g), calludase complay (50 EBU (g)				
Hemicellulose: 23.21%	- Grinding to obtain powder	50 °C, 150 rpm, substrate concentration 10%, 24 h	Hemicellulose: 19.66%	2.5% rice straw, 0.1 M sodium citrate buffer, pH 4.8, 0.02% sodium	N.D.	N.P.	N.D.	[80]
Lignin: 15.79%)		 Washing until neutral pH Drying (60 °C, 24 h) 	Lignin: 10.77%	azide, 50 °C, 150 rpm, 72 h				
Rice straw			After NMMO:					
(<u>Cellulose</u> : 40.2%	Milling (178, 852 um)	Two treatments: NMMO and Phosphoric acid (PA)	<u>Cellulose</u> : 43.5%	Enzymatic hydrolysis:	<u>NMMO</u> :	Preculture <i>M. indicus</i> (32 °C, 24 h) Inoculation + incubation	<u>NMMO</u> :	
<u>Hemicellulose</u> : 12.5%	- Drying (RT)	<u>Chemical NMMO:</u> NNMO (85%, ratio 1:9), 120 °C, 3 h - Addition DI water (60 mL)	Hemicellulose: 11.2%	(<i>Novozymes</i>), 20 FPU/g, 15% solid loading, 72 h, 45 °C, sodium citrate buffer (pH 4.8, 0.05 M)	<u>Glucose</u> : >100 g/L	fungal spores (48 h, 32 °C) Spore suspension (anaerobic fermentation24 h, 32 °C) SETE \sim (L M indiana	44.2 g/L	[82]
Lignin: 16.7%)		- Washing with boiling water	Lignin: 13.2%	d and a second se		$\frac{351}{37}$ °C, anaerobic		
Rice straw	 Oven-drying (80 °C) Blending (20-mesh sieve) 	<u>Chemical</u> : [EMIM]Ac Optimization by RSM (Optimal: 5% loading ratio, 128.4 °C, 71.83 min) - Water bath (5 min, RT) - Washing with DI water - Oven-drying (80 °C)	N.D. ¹	Enzymatic hydrolysis: Celluclast 1.5 L (20 FPU/g), 40 μL sodium azide, 2.5% biomass, 72 h, 45 °C, 0.05 M citrate buffer, pH 4.7, 200 rpm	<u>Total RS</u> : 57.3 mg/ 100 mg biomass	<i>S. cerevisiae</i> inoculum (1 mL), 30 °C, 72 h, 150 rpm	5.9 g/L	[81]
Rice straw	Air-dryingChopping and milling	<u>Chemical</u> : 1% NaOH, 10% solid loading Washing until neutral pH	N.D. ¹	<u>Saccharification</u> : Accellerase®1500 or Celluclast (24–48 h)	Total sugars: 21.66 g/L	Unconventional yeast precult. (MGYP, 30 °C, 72 h) <u>Fermentation</u> : 30 °C, 48 h	3.32 g/L (<i>P. stipitis</i> NCIM349, 48 h)	[78]

Table 4. Summary of recent experiments done for pretreatment of rice straw.

¹ N.D. = Not determined, ² N.P. = Not performed.

As S. cerevisiae is a hexose-fermenting yeast [88], the issue of xylose fermentation was already addressed by many studies that have used xylose-fermenting microorganisms such as P. stipitis [79,83,89] and Spathaspora passalidarum [90], to further increase ethanol concentration. The use of *P. stipitis* for the fermentation of rice straw has allowed the production of 3.32 g/L of ethanol after 48 h [78]. While this yeast is able to ferment both glucose and xylose, the presence of glucose hinders, in a non-competitive manner, the transport of xylose [89]. The faster utilization of glucose by P. stipitis was observed in an early study, in which a specific strain of *P. stipitis* produced ethanol from glucose at a higher rate than from xylose. However, a slightly lower ethanol yield was obtained from this strain (22.7 g/L from a glucose medium (60 g/L) versus 24.3 g/L from a xylose medium (60 g/L)) [91]. Valuable information to note is that, in the latter experiment, 22.7 g/L of ethanol from glucose were produced after 96 h of fermentation, and 24.3 g/L of ethanol from xylose were obtained after 120 h of fermentation, as opposed to 48 h (with only 4.6% total sugars) [78]. In another experiment [92], designed *P. stipitis* strains were constructed for second-generation ethanol production from lignocellulosic biomass hydrolysates. The ethanol concentrations obtained following fermentation using those specific strains, which were constructed to further enhance xylose fermentation, were not reported. However, it was declared that these strains are more resistant to inhibitors, which is similar to an observation previously made [78]. On another note, there have been other recent applications of non-conventional yeasts for bioethanol production, such as the use of Spathaspora passalidarum [90]. Fermentation by S. passalidarum was evaluated in both synthetic medium and maple hydrolysate and has allowed a maximum production of 40 g/L of ethanol after 38 h of fermentation of synthetic medium, as opposed to 38 g/L of ethanol after 59 h of fermentation of maple hydrolysate by a mutant strain (E7). However, it is important to note that even the maple hydrolysate was supplemented with CBS, hence increasing the cost of the process.

5. Pretreatment of Wheat Straw

Raw wheat straw composition varies between 33–42% for cellulose (db), 17–30% for hemicellulose (db), and 17.5–28% lignin (db), as it exists in different varieties [93]. Before pretreatment, the biomass is prepared through drying and particle size reduction.

Wheat straw was then pretreated chemically using [TEA][H₂SO₄] [94] or a deep eutectic solvent (DES) [95]. Both agents were especially beneficial in removing lignin, decreasing the content from 18.8% to 3.73% and from 18.58% to 8.09%, respectively, while significantly increasing cellulose content from 35.69% to 53.52% and from 33.02% to 68.29%, respectively. On a different note, thermochemical pretreatment using subcritical water [96] and microwave-assisted NaOH pretreatment [97] were also applied to wheat straw. Both processes were optimized by RSM, with respective optimal conditions of (220.51 °C, 22.01 min, 2.5% solid loading) and (160 °C, 15 min, 1.5% NaOH, 10% solid loading). Subcritical water increased cellulose content from 36.97% to 62.89%, while paradoxically increased lignin content significantly (from 27.66% to 36.47%); this phenomenon can be explained by the deformation of already-existing lignin linkages and the formation of new linkages within the complex structure. In contrast, microwave-assisted NaOH treatment exhibited a successful decrease in lignin content from 17.83% to 7.66% and an increase in cellulose content from 41.72% to 74.15%. While alkaline pretreatment has repeatedly been presented as a promising pretreatment technique [98], its assistance by microwaves has further enhanced the pretreatment because microwaves heat up the polar components within the biomass [99], which will consequently disrupt the complex structure and thus improve hydrolysis. The experiments are summarized in Table 5.

Raw Materials	Biomass Preparation	Pretreatment	Composition (Treated; % db)	Saccharification	Reducing Sugars	Fermentation	Bioethanol	References
Wheat straw(Cellulose: 36.97%)Hemicellulose:20.17 %Lignin:27.66%)	 Cutting (3–5 cm) Crushing (60-mesh) Drying (45 °C, 24 h) 	 <u>Thermomechanical</u>: Subcritical water treatment Optimization by RSM (Optimal: 220.51 °C, 22.01 min, 2.5% solid loading) 	<u>Cellulose</u> : 62.89% <u>Hemicellulose</u> : 1.80 % Lignin: 36.47%	Enzymatic hydrolysis: 5 cellulase mixes 20 FPU/g, β-glucosidases 1 U/g, 50 °C, 120 rpm, 96 h, 15% solid loading	<u>Glucose</u> : 80.81 g/L	<i>S. cerevisiae</i> preculture (YPD, 30 °C, 150 rpm, 24 h,) <u>SHF</u> : 10% inoculum, 30 °C, 48 h	37 g/L (64 h)	[96]
Wheat straw (<u>Cellulose</u> : 41.72% <u>Hemicellulose</u> : 19.98% <u>Lignin:</u> 17.83%)	 Size reduction (1–3 cm) Drying 	 Physicochemical: MW+ NaOH Optimization by RSM (Optimal: 160 °C, 15 min, 1.5% NaOH, 10% w/v biomass loading) Washing (DI water) Drying (70 °C, 6 h) Milling (100–200 μm) 	<u>Cellulose</u> : 74.15% <u>Hemicellulose</u> : 5.44% Lignin: 7.66%	Microbial hydrolysis: (<i>Bacillus</i> sp. BMP01, 30 °C, 14 days)	<u>Total RS:</u> 718 mg/g _{WS}	<i>S. cerevisiae</i> and <i>Zymomonas</i> <i>mobilis</i> precultures (YPG, 30 °C, 24 h) <u>Fermentation</u> (108 h, 120 rpm, 30 °C)	Ethanol yield: 68.2% (96 h)	[97]
Wheat straw (<u>Cellulose</u> : 35.69% <u>Hemicellulose</u> : 29.68% <u>Lignin:</u> 18.8%)	- Washing - Drying (50 °C) - Grinding (< 0.6 mm)	<u>Chemical</u> : 8 g [TEA][H ₂ SO ₄] melted at 130 °C, 2 g water (1:5 ratio), 130 °C, 3 h	<u>Cellulose</u> : 53.52% <u>Hemicellulose</u> : 10.55% <u>Lignin:</u> 3.73%	Enzymatic hydrolysis: Cellulase CelluMax GFL (<i>Novozymes</i>), 0.05 M sodium citrate, pH 4.8, solid-liquid ratio 1:20, 28 FPU/g residue biomass, 0.2% sodium azide, 72 h, 50 °C, 200 rpm - Evaporation, 50 °C	<u>Glucose</u> : 35 g/L <u>Xylose:</u> 6 g/L	<i>S. cerevisiae</i> preculture (YPD) <u>Fermentation</u> : 3 g inoculum, 30 °C, 96 h	43.1 g/L	[94]
Wheat straw (<u>Cellulose</u> : 33.02% <u>Hemicellulose</u> : 17.26% Lignin: 18.58%)	Washing (DI water) Drying, crushing Sieving (60-mesh sieve)	<u>Chemical</u> : DES (solid-liquid ratio 1:15, 1 h, 120 °C) Vacuum filtration Washing	<u>Cellulose:</u> 68.29% <u>Hemicellulose</u> : 3.94% <u>Lignin:</u> 8.09%	Enzymatic hydrolysis: Celluclast 2 L (Novozymes), 50 °C,150 rpm, 11.4 FPU/g	<u>Glucose</u> : 48.05 g/L Xylose: 2.26 g/L	<u>SHF</u> : Optimization by RSM (Optimal: 18 h, Angel Yeast 10% v/v, 40 °C, 120 rpm)	15.42 g/L	[95]

Table 5. Summary of experiments done for the pretreatment of wheat straw.

Moreover, Separate Hydrolysis and Fermentation (SHF) was performed [95,96], yielding 80.81 g/L of glucose, and 48.05 g/L and 2.26 g/L of xylose; it is interesting to note that, although lignin content has increased [96], the sharp decrease in hemicellulose content (from 20.17% to 1.80%) may have played a significant role in the reduction of recalcitrance of wheat straw to enzymatic hydrolysis, thus making cellulose more available for the enzymes. In addition to SHF, enzymatic hydrolysis was achieved and followed by the concentration of the hydrolyzed sample by evaporation at 50 °C [94]; this procedure has led to obtaining 35 g/L of glucose and 6 g/L of xylose, which are in accordance with the level of available cellulose after pretreatment. Another saccharification technique applied to wheat straw is microbial hydrolysis using the bacterium *Bacillus* sp. BMP01 [97]. The latter was performed over 14 days at a temperature of 30 °C and resulted in a maximum total reducing sugar concentration of 0.718 g/gws on the eighth day; this indicates that the hydrolysis conditions are not the most suitable for hydrolysis of the available cellulose content.

Finally, after the fermentation step of the SHF processes, the obtained ethanol concentrations were 37 g/L [96] and 15.42 g/L [95]. The difference in concentrations could be attributed to fermentation temperature, as 30 °C [96] is more favorable for fermentation than 40 °C. However, this latter temperature was chosen as optimal, since the fermentation was optimized using RSM and its optimal conditions were (18 h, 10% Angel Yeast, 40 °C, 120 rpm) [95]; this indicates that a revision of the experimental design be done so that the temperature becomes more favorable of fermentation. Fermentation using S. cerevisiae of $[TEA][H_2SO_4]$ -treated and hydrolyzed samples allowed the production of 43.1 g/L of ethanol which highlights the efficiency of pretreatment and hydrolysis. Finally, the microbially-hydrolyzed samples were fermented by both S. cerevisiae (a hexose-fermenting yeast) and Zymomonas mobilis (a pentose-fermenting bacterium) was accomplished [97] to ferment both glucose and xylose. The recorded ethanol yield was of 68.2% at 96 h of fermentation, whereas the duration of the process was of 14 days (336 h). Considering that the total amount of reducing sugars obtained was not as significant as the available cellulose before microbial hydrolysis, it is justifiable as to why 68.2% is possibly the highest recorded yield.

Regarding lignin removal, it is clear that [TEA][H₂SO₄] proved to be the most effective. Using the latter pretreatment and performance of enzymatic hydrolysis leads to an important glucose concentration which will be beneficial for subsequent fermentation. However, the degradation of hemicellulose and the increase in lignin content following subcritical water pretreatment have revealed that even though the barrier induced by lignin was not eliminated, recalcitrance can still be reduced with the significant removal of hemicellulose.

6. Pretreatment of Sugarcane Bagasse

The composition of sugarcane bagasse (SCB) ranges between 33–49% cellulose (db), 19–21.5% hemicellulose (db), and 24.5–29.5% lignin (db); the variability caused by the presence of various varieties of sugarcane [100]. Like most LCBs, sugarcane bagasse is often subject to drying and/or particle size reduction prior to pretreatment.

SCB was subjected to sulfuric acid-based pretreatment [101], three-step hydrothermalchemical pretreatment [102], and liquid hot water pretreatment [103]. The sulfuric acidbased treatment was followed by an optimized autoclave treatment of optimal conditions (120 °C, 60 min, 33.3% solid loading, 0.05 g/g acid dosage). The advantages of autoclave pretreatment could be to remove the moisture content from the pretreated samples, as moisture was not previously eliminated during biomass preparation. Moreover, SCB was subjected to a three-step pretreatment that first begins with treating the samples using a pressure reactor at 183 °C for 41 min. The biomass is then subject to a chemical pretreatment with 0.2 mol/L NaOH, and finally undergoes an advanced chemical pretreatment using NaOH and H₂O₂. The latter was optimized by creating a Design of Experiments (DOE) that revealed the following optimal conditions: 30 g biomass, 0.3 g_{H2O2}/g_{SCB}, 5 mol/L NaOH, 9.67 mL/g, 8 h. As a result of the advanced pretreatment, cellulose content increased from 48.7% to 78.91%, while lignin and hemicellulose decreased from 24.81% to 17.6% and from 21.14% to 7.13%, respectively. Finally, SCB was subjected to liquid hot water (LHW) pretreatment optimized by RSM (optimal conditions: 0.05 M H_2SO_4 , 160 °C, 60 min). The remarkable outcome of this pretreatment was the outstanding removal of hemicellulose, as its content decreased from 19.2% to 0.59%, as opposed to lignin content which decreased from 29.2% to 23.5%. Furthermore, cellulose content was not enhanced following pretreatment, and was on the contrary slightly decreased (from 33.1% to 29.4%); it can be concluded that the three main components of SCB biomass are sensitive to LHW pretreatment. The results were summarized in Table 6.

For the saccharification step, SCB was subject to two consecutive hydrolyses [101], enzymatic hydrolysis [102], and SSF [103]. The first hydrolysis step was conducted for 18 h at low solid loading (3%), while the second was done with 30% solid loading, greater enzyme dosage (20 mg/g), and lasted 72 h. The outcomes of this two-step saccharification were 95.81 g/L of glucose and 79.73 g/L of xylose. While it has been reported that higher solid loadings enhance sugar and consequent ethanol production [104], it has also been reported that such higher solid loadings affected the conduct of certain enzymes [104] just like it faces certain obstacles that do not concern lower-solid loading hydrolyses [104]. Hence, it can be hypothesized that a first, low-solid enzymatic hydrolysis was performed in order to ensure an efficient enzyme activity and to maintain a suitable water content [104] before increasing the solid loading; it is worth noting however that the solid loading was gradually increased from 20 to 30%. Furthermore, the advanced chemical pretreatment of SCB was followed by enzymatic hydrolysis that yielded 60.9% of overall glucose [104], while the LHW-treated samples were followed by SSF whose saccharification step yielded 96.86% glucose [103]. The overall glucose yield groups the responses of the various pretreatments into a single value, representing the efficiency of all three consecutive pretreatments, as opposed to the efficiency of the single LHW pretreatment.

Finally, SCB has undergone Fed-Batch and Enzyme-SSCF [101] fermentation using different yeast strains [102], and fermentation as part of SSF [103]. FBE-SSCF was conducted using *S. cerevisiae* for 120 h (30% solid loading, 34 °C), which yielded 77.51 g/L of ethanol; this concentration is higher than the greatest ethanol concentration obtained by SSF (19.9 g/L), at 72 h after fermentation. On the other hand, three yeast strains were tested for fermentation, and the strain labeled LBCM1047 yielded 37 g/L of ethanol.

The results indicate that the chemical sulfuric acid treatment was the most efficient, especially in terms of cellulose availability for enzymatic hydrolysis, which inevitably enhanced fermentation. However, and as observed with [TEA][H₂SO₄] pretreatment of wheat straw [94], the important removal of hemicellulose [103] has still allowed efficient hydrolysis and fermentation of the conserved cellulose, regardless of the feeble de-lignification ability.

Raw Materials	Biomass Preparation	Pretreatment	Composition (Treated; % db)	Saccharification	Reducing Sugars	Fermentation	Bioethanol	References
Sugarcane bagasse	Milling (3 mm)	<u>Chemical</u> : Sulfuric Acid (0.5 g water/g dry biomass) Pelletization (200 mm) Air drying (RT) Autoclave (Optimal: 120 °C, 60 min, solid loading 33.3%, 0.05 g/g acid dosage)	N.D.	Low solid loding hydrolysis: Cellic CTec2 (<i>Sigma Aldrich</i>), 10 mg/g _{glucan} , 50 °C, 250 rpm, pH 4.8, 18 h Enzymatic hydrolysis: 30% solid loading, 72 h	<u>Glucose</u> : 95.81 g/L Xylose: 79.73 g/L	S.cerevisiae preculture (YPX, 30 °C, 250 rpm) Fed-Batch and Enzyme (FBE)-SSCF:34 °C, 150 rpm, 120 h, pH 5.5–6, solid loading 30%	77.51 g/L	[101]
Sugarcane bagasse (<u>Cellulose</u> : 33.1% <u>Hemicellulose</u> : 19.2% <u>Lignin</u> : 29.2%)	Oven-drying (50 °C, 24 h) Grinding (0.061–0.25 mm) Oven-dried (105 °C, 5 h)	Physicochemical: Optimization by RSM (Optimal: 0.05 M H ₂ SO ₄ , 160 °C, 60 min)	<u>Cellulose</u> : 29.4% <u>Hemicellulose</u> : 0.59% Lignin: 23.5%	- Enzymatic hydrolysis: Cellic CTec2 (<i>Novozymes</i>) 5% substrate <i>w/v</i> (25 FPU/g), 50 mM sodium citrate buffer pH 4.8, 1% sodium azide, 150 rpm, 50 °C, 72 h	<u>Glucose yield:</u> 96.86%	<i>S. cerevisiae</i> preculture (30 °C, 24 h in agar) <u>then</u> YPD, 35 °C, 150 rpm <u>SSF</u> : pH 4.8, 6.25% remaining solid residue	19.9 g/L (72 h)	[103]
Sugarcane bagasse (<u>Cellulose</u> : 48.7% <u>Hemicellulose</u> : 21.14% <u>Lignin:</u> 24.81%)	- Sunlight drying (15 days)	Hydrothermal:183 °C, 41 min, liquid-solid ratio3.94 mL/g, 11.7 barPressing (9 tons pressure)Chemical:Oven-drying (55 °C,12 h)Grinding (0.42 mm)NaOH (aq, 0.2 mol/L),liquid-solid ratio 10 mL/g,2800 rpm, 30 sAdvanced chemical:Optimization by DoE (30 g,0.3 gH202/gSB, 5 mol/L NaOH, pH 11.6,150 rpm, 25 °C, liquid-solid ratio9.67 mL/g, 8 h)Blending (2800 rpm, 30 s)	Advanced chemical: Cellulose: 78.91% Hemicellulose: 7.13% Lignin: 17.6%	Enzymatic hydrolysis: Residual solid fraction (1 g), 0.05 M citrate buffer, pH 4.8, 0.02% sodium azide, 15% Cellic HTec2 and 85% Cellic CTec 2 (cellulase 10 FPU/g, β-glucosidase 52.21 U/g), liquid-solid ratio 10 mL/g, 72 h, 150 rpm, 50 °C	<u>Overall Glucose</u> <u>Yield:</u> 60.9%	<i>S. cerevisiae</i> strains: two commercial yeasts (mills), one yeast (distillery), 34 °C, 150 rpm	37 g/L (LBCM1047 strain) 190.8 L _{ethanol} per ton of pretreated biomass	[102]

Table 6. Summary of experiments done for the pretreatment of sugarcane bagasse.

7. Pretreatment of Other Biomasses

Barley straw, bamboo, rye stillage, and Eucalyptus sawdust (Table 7) are all subject to drying and particle size reduction before pretreatment.

Table 7. Chemical composition of other selected lignocellulosic biomasses.

Barley straw	32.0-43.0	20.0-33.0	6.0–20.0	[26,105,106]
Bamboo residue	40.0-73.83	12.49–30	10.0–33.0	[107,108]
Eucalyptus sawdust	43.0–54.1	11.0–18.4	21.0-34.0	[26,109,110]

Steam explosion (SE) is a common pretreatment technique used to treat Barley Straw [105,106]. However, this biomass was also pretreated using extrusion [111]. SE optimized by RSM was performed at 160 °C for 30 min, at a concentration of phosphoric acid equal to 2.88% w/v [106,112]. The slurries were then either filtered or detoxified, and the solid fraction was finally oven-dried at 38 $^{\circ}$ C. On the other hand, regular SE applied to barley straw with 10% moisture, was performed at 180 °C for 30 min, at a pressure of 10 bar [105]. The composition of the resulting solid fractions, or water-insoluble solids (WIS) fractions, is then analyzed. In contrast, extrusion pretreatment of barley straw was performed using 7.2% *w/v* NaOH, 2.5% *w/v* H₂SO₄, at 100 °C and 120 rpm, for 3 h [111]. Rye stillage was subject to optimized microwave-assisted acidic pretreatment [113], with optimal conditions (300 W, 0.2 M H₂SO₄, 54 PSI, 15 min). Bamboo residues, on the other hand, were subjected to chemical pretreatment using a hydrogen peroxide—Acetic acid (HPAC) solution, at 60 $^{\circ}$ C, and for 2 h [107]. Finally, Eucalyptus sawdust was also subject to steam explosion (10 min, 200 °C), with or without NaOH impregnation [109]; this treatment consists of impregnating the samples with NaOH for 30 min, and conditioning them for 20 h at 23 °C. The operation was followed by filter pressing (20 MPa) and oven-drying for 48 h. Alkaline impregnation is a process by which a mobile front separates a reacted outer region from an intact inner zone [114]. The use of NaOH impregnation was to inhibit the autohydrolysis of solids when subject to SE.

Following pretreatment, efficient de-lignification was observed, with a decrease from 16.26 to 12.62% [106] and from 32.41 to 9.28% [107]. While SE has successfully decreased lignin content of barley straw [106], an important increase in lignin content of barley straw was notably be observed, with an increase from 16.8% to 30.7% [105]. Furthermore, the extrusion pretreatment of barley straw also slightly increased lignin content, from 18.8% to 20.82% [111]. The temperature of the effective SE treatment (160 °C) was lower than the treatment during which lignin increased (180 °C), which indicates that a higher temperature might induce the formation of new linkages in barley straw, hence rendering the pretreatment less efficient in the de-lignification process. Similarly, the extrusion process has not degraded lignin from barley straw. Regarding bamboo residues, significant delignification was observed (from 32.41% to 9.28%), in addition to an increase in cellulose content (from 40.94% to 65%), thus indicating the effectiveness of HPAC for the pretreatment of bamboo residues. Finally, physico-chemical pretreatment of Eucalyptus sawdust has efficiently increased cellulose content from 43.6% to 60.1% but has also significantly increased lignin content from 30.5 to 46.4%.

Saccharification of the biomasses was performed either through enzymatic hydrolysis [106,107,109,112,113] or by bioextrusion [111]; it is important to note that simultaneous saccharification and fermentation (SSF) of pretreated biomasses was performed, yielding 50 g/L [105], 38 g/L [111], and 75.6 g/L [109]. Regular fermentation of the selected biomasses yielded 16 g/L [113] and 13 g/L [107]; this shows that SE pretreatment ensures efficient saccharification, and thus high ethanol yields. While some pretreatments have increased lignin content, the enzymatic hydrolysis conditions used proved to be effective, which indicates that while new linkages might have been formed, there has been a restructure that increased the enzyme's accessibility for adequate hydrolysis. Table 8 summarizes the experiments done for the pretreatment of other lignocellulosic biomasses.

Raw Composition Saccharification **Biomass Preparation** Pretreatment **Reducing Sugars** Fermentation Bioethanol References Materials (Treated; %db) Composition of **Barley Straw** water-insoluble solid fraction Physico-chemical: Steam explosion (Optimal (Cellulose as glucose: (WIS): 42.27% conditions: 160 °C, 30 min, 2.88 w/v Maximum phosphoric acid concentration) Glucose: Enzymatic hydrolysis (for SHCF): Co-fermentation: attainable - Air drying Glucose yield: 65.11% Hemicellulose 50 °C, 150 rpm, pH 4.8, 15 FPU/g E. coli SL100, 37 °C, vield [112] - Filtration or detoxification of slurry -Milling (1 cm) 90% as xylose: substrate enzyme loading, 72 h 150 rpm, pH 6.5 $(Y_{Emax}) =$ Detoxification of liquid prehydrolysate Xylose: 30.23% 89.1% (5 M NH₄OH; centrifugation 5000 rpm) 3.72% Oven-drying of solid fraction at 38 °C. Lignin: Lignin: 16.26%) 12.62% Rye stillage (Cellulose: Enzymatic hydrolysis: Physico-chemical: Microwave (Optimal S. cerevisiae 16.8% Cellic[®] CTec2, 1 FPU/g, 50 °C, pH N.P.² conditions: 300 W, $N.D.^1$ 156 mg/g (2 g/L) $\approx 16 \text{ g/L}$ [113] Hemicellulose: 5.5, 70 rpm, 35 °C, 72 h 0.2 M H₂SO₄, 54 PSI, 15 min) 29.62% 24 h Lignin: 15.57%) **Barley straw** WIS fraction: S. cerevisiae (0.25 g/L (Cellulose: Cellulose: inoculum) 55.8% Enzymatic hydrolysis (for PSSF): 32.9% Drying till 10% Physico-chemical: Steam Explosion (particle Cellic[®] CTec2, 30 FPU/g enzyme Fermentation (for PSSF): $N.D.^1$ $\approx 50 \text{ g/L}$ [105] Hemicellulose: moisture size 6–10 mm, 180 °C, 30 min, 10 bar) Hemicellulose: loading, 8 h, 50 °C, 20% w/v solid 35 °C, 48 h 27.2% 10.3% concentration - Washing and drying at 60 °C Lignin: Lignin: 30.7% 16.8%) Barley straw Glucose: Cellulose: Thermo-mechanical/Chemical: 30.94% IF, **Bioextrusion:** 32.61% (Cellulose: 3.35% SF Sequential alkaline extrusion; 7.2% w/v 0.9 kg/h dry extrudate, Cellic® Drying till 11.4% 33.2% NaOH, 2.5% w/v H₂SO₄, biomass flow CTec2, 0.02 M citrate buffer, pH 4.8, moisture Hemicellulose: Fermentation (LSSCF): Yeast Xylose: 10.72% IF, 38 g/L 2 kg/h, 100 °C, 120 rpm, NaOH-catalyzed 7.5 FPU/g enzyme loading, [111] Crushing (size Hemicellulose: 18.56% (1 g/L), 30 °C, 150 rpm, 72 h. extrusion 3 h 0.7 L/h, liquid-solid ratio 3 6.58% SF 2 mm) 20.9% Lignin: Oven-drying of part of extrudate 45 °C, 2 h LSSCF Arabinose: Lignin: 20.82% 1.88% IF, 1.24% SF 18.8%)

Table 8. Summary of experiments done for the pretreatment of other lignocellulosic biomasses.

Table 8. Cont.

Raw Materials	Biomass Preparation	Pretreatment	Composition (Treated; %db)	Saccharification	Reducing sugars	Fermentation	Bioethanol	References
P. amarus bamboo residues (<u>Cellulose</u> : 40.94% <u>Hemicellulose</u> : 18.48%	Grinding	<u>Chemical</u> : Hydrogen peroxide-acetic acid (HPAC); HPAC solution 1:1 <i>v/v</i> , 0.5% <i>w/w</i> sulfuric acid, 60 °C, 2 h - Filtration, washing, drying (50 °C)	<u>Cellulose</u> : ≈65% <u>Hemicellulose</u> : ≈18% Lignin:	Enzymatic hydrolysis: 5% substrate concentration w/v, 10 FPU/g enzyme loading, 50 °C, pH 4.8, 150 rpm, 72 h	<u>Glucose</u> : 79.31% Xylose: 85.53%	<u>Fermentation</u> : 35 °C, 90 rpm, 24 h	≈13 g/L	[107]
Lignin: 32.41%)			9.28%					
Eucalyptus sawdust		Chemical: NaOH impregnation for some samples (1:4 solid-liquid ratio), 30 min, conditioning (23 °C, 20 h)Kiln-drying at 40 °Cconditioning (23 °C, 20 h) Filter pressing (20 MPa)Particle sizes (>2 mm, 1-2 mm, 0.5-1 mm,Solar oven-drying: 48 h Physio-chemical: Steam Explosion: 10 min, 200 °C	Solid fraction; (-) NaOH impregnation	Enzymatic hydrolysis (for SSF): Cellic [®] CTec 2, 27% solid loading, 25 FPU/g enzyme loading, 96 h, pH 4.8, 50 °C, 150 rpm	Enzymatic hydrolyzates: (-) NaOH impregnation <u>Glucose:</u> 134 g/L	<u>Fermentation</u> (for SSF): 27% solid suspension, 30 °C, 100 rpm, 48 h	75.6 g/L	[109]
(<u>Cellulose</u> : 43.6%	 Kiln-drying at 40 °C Particle sizes (>2 mm, 1-2 mm, 0.5-1 mm, < 0.5 mm) 		<u>Cellulose</u> : 60.1%					
Hemicellulose: 11.1%			<u>Hemicellulose</u> : N.D.					
Lignin: 30.5%)		Filter pressing (20 MPa) Washing and filter pressing	Lignin: 46.4%					

¹ N.D. = Not determined, ² N.P. = Not performed.

8. Ethanol Production Overview

To reiterate, a high ethanol titer equal to 76.92 g/L was obtained from the fermentation of chemically pretreated industrial hemp using NaOH and process optimization [59], just as an ethanol concentration of 70.6 g/L was obtained from chemically and thermally pretreated corn stover using $Ca(OH)_2$ and an autoclave [71]. In contrast, 44.2 g/L of ethanol was produced from the fermentation of chemically pretreated rice straw using NNMO [82], in addition to 43.1 g/L of bioethanol produced following fermentation of chemically treated wheat straw using [TEA][H₂SO₄] [94]. As for sugarcane bagasse, a high ethanol concentration of 77.51 g/L was produced from chemical and optimized thermal pretreatment of the biomass [101]. Among the different pretreatments of barley straw, an ethanol concentration of 50 g/L was obtained from steam-exploded biomass [105], while about 16 g/L were obtained from microwave pretreated rye stillage, 13 g/L of ethanol from bamboo residues, and 75.6 g/L of steam-exploded Eucalyptus sawdust [108,110,114]; these recent experiments highlight once again the efficiency of chemical pretreatment of lignocellulosic biomasses; they also confirm the possibility of obtaining high ethanol concentrations from these biomasses, thus confirming its importance as an alternative energy source.

9. Conclusions

Lignocellulosic biomasses are a promising resource for biofuel production, and numerous attempts for their pretreatment have already been elaborated. Chemical pretreatment remains the most efficient to this day: NaOH remains the most effective chemical agent in hemp biomass pretreatment, lime the most efficient chemical agent for corn stover pretreatment, NMMO was the most efficient chemical agent for the pretreatment of rice straw, [TEA][H₂SO₄] proved to be the most effective for wheat straw pretreatment, and finally sulfuric acid performed best in sugarcane bagasse pretreatment; it is important however to conduct fermentation trials to confirm further the efficiencies of both, the pretreatments and the saccharification processes. The use of non-conventional microorganisms for fermentation was also showcased, which reveals greater measures to expand in order to further enhance results; it is also important to look deeper into the pretreatments' impact on the environment, their energy consumption, their costs, and their use at larger manufacturing scales. In fact, the industrialization of lignocellulosic ethanol has already begun, with many countries having already installed plants. Nevertheless, to achieve this industrialization, manufacturers are faced with diverse obstacles: (1) more profound understanding of raw materials, their properties, their restrictive factors during pretreatment (inhibition, mass transfer, etc.), (2) development of low-cost enzymatic hydrolysis technique with optimum performance, and (3) a deeper understanding of microorganisms and their metabolic activities to enhance fermentation efficiency further, which also includes the engineering of specific strains. Therefore, when it comes to pretreatment efficiency and the subsequent fermentation outcomes, chemical pretreatment remains the most effective for bioethanol production; it is possible that non-chemical pretreatment techniques be taken to an industrial scale, but more in-depth research is required to surmount the challenges faced.

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