

Pretreatments Applied to Wheat Straw to Obtain Bioethanol

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Abstract: This work is a comprehensive study focusing on various methods for processing wheat straw to enhance its suitability for bioethanol production. It delves into mechanical, physical, chemical, and biological pretreatments, each aimed at improving the enzymatic hydrolysis and fermentation processes necessary for bioethanol production. Mechanical and physical pretreatments involve reducing the size of wheat straw to improve enzymatic hydrolysis. Physical methods include heating and irradiation, which alter the structural properties of wheat straw. Chemical pretreatments involve using acids, alkalis, and organic solvents to remove lignin and hemicellulose, making cellulose more accessible for hydrolysis. Biological pretreatments utilize microorganisms and fungi to degrade lignin and other complex compounds, enhancing the breakdown of cellulose. The study presents data on the effectiveness of these treatments in terms of lignin removal, sugar yield, and overall bioethanol production efficiency. The research is aligned with the global move towards renewable energy sources and emphasizes the importance of utilizing agricultural waste, like wheat straw, for sustainable energy production.

Keywords: bioethanol; lignocellulosic biomass; pretreatments



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1. Introduction

Energy from renewable sources is at the heart of the priorities of the European Green Deal. Directive (UE) 2018/2002, regarding the promotion of the use of energy from renewable sources [1], is a central element of the EU's energy policy and a key factor in achieving the renewable energy targets by 2030, when at least 32% of energy should be from renewable sources [1].

An important target set out in the Climate Action Plan under the European Green Deal [2] is to reduce greenhouse gas (GHG) emissions by 55% by 2030. To achieve this target, the EU has set a balanced path towards climate neutrality by 2050 through decarbonizing all sectors of the economy. In this sense, a transition from the current energy system to an integrated energy system based largely on renewable sources is necessary. As specified in the impact assessment related to the plan for achieving the climate objective, for the 55% reduction in greenhouse gases, the share of energy from renewable sources in 2030 will have to reach 38–40% [2]. According to the estimates of the European Environment Agency (EEA), in 2022 renewable energy represented 23.0% of energy consumed in the EU, up from 21.9% in 2021. In addition, the EU as a whole is above the slightly more ambitious trajectory defined by the Member States themselves in their National Renewable Energy Action Plans (NRAPs) [3]. In recent years there has been a continuous increase in the overall share of renewable energy sources (RES) at the EU level and the sectoral share of energy from renewable sources of electricity (E-SRE), heating and cooling, and (to a lesser extent) from transport (T-SRE).

Overall, bioenergy continues to be the main renewable energy source in the EU. Solid biofuels account for 68.4%, the largest share of bioenergy. Of these solid biofuels, forestry

accounts for about 91%. The other forms of bioenergy consist of liquid biofuels (12.6%), biogas (11.6%), the renewable share of municipal waste (7.2%), and coal (2%) [4].

Globally, bioethanol production is mostly involved in elements of cereal manufacturing, such as corn and sugarcane. According to the data in Figure 1, the largest production of bioethanol was in the United States, followed by Brazil.

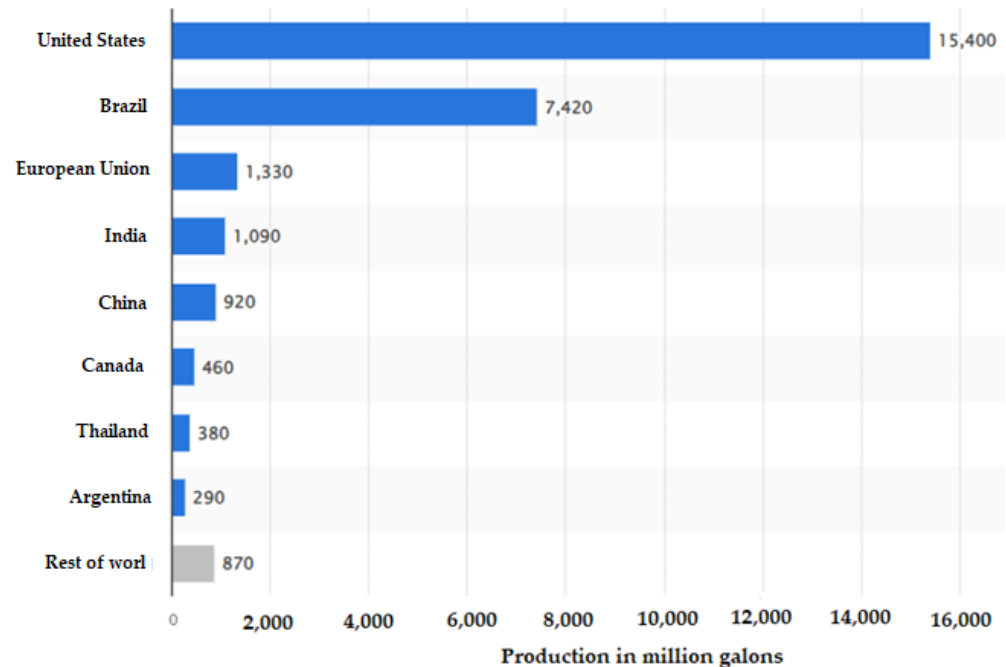


Figure 1. Global bioethanol production in 2022 expressed in billions of gallons (adapted from [5]).

The use of biofuels allows for a reduction in greenhouse gas emissions of up to 95% compared to fossil fuels. This target is in line with the United Nations' targets for reducing greenhouse gas emissions.

Globally, the land surface occupied by agriculture is between 10 and 12% [6]. Worldwide, approximately 354 million tons of wheat straw are produced annually, which can represent raw material for energy sources, reducing the use of fossil fuels [6–9]. Additionally, 40% of CO₂ emissions result from agriculture [10].

In the context of the circular bioeconomy, given the climate changes and the increase in pollution, environmentally friendly energy sources are sought, and so agricultural straws are of interest due to their valorization and transformation into bioethanol [9].

To reduce environmental pollution, renewable energy must be utilized using waste obtained from agricultural production. The ratio of lignin, hemicellulose, and cellulose in the content of wheat straw is 3:3:4 [11].

Wheat straw, due to its hemicellulose and cellulose content, is a raw material for the production of bioethanol, which is a clean fuel that can replace gasoline, reducing CO₂ emissions from car engines [6,7].

Biofuels are liquid or gaseous fuels, such as biodiesel, bioethanol and biogas, which are made from plants [12–18].

Part of the wheat straw is used as animal feed, while the rest of the straw is burned in the field, increasing air pollution [19–22].

Overall, 442 billion liters of bioethanol can be obtained from lignocellulosic biomasses, and 491 billion liters of bioethanol can be obtained annually from total crop residues [23].

The following processes are necessary: pretreatment, enzymatic hydrolysis and fermentation. For the production of bioethanol, the cellulosic material from agricultural residues is collected from the field and transported to the factory that uses them for the production of bioethanol [24].

The European Commission has called for a 90% reduction in emissions in EU countries by 2040, which will require an extensive and emission-free supply system within 16 years and an 80% reduction in the use of fossil fuels for energy [25].

The commission has also set a target of 45% of renewable energy sources to be utilized in the EU's energy mix by 2030 [26].

This paper reviews the pretreatment methods of wheat straw to obtain bioethanol. The work is a comprehensive study focusing on various methods for processing wheat straw to enhance its suitability for bioethanol production. It delves into mechanical, physical, chemical, and biological pretreatments, each aimed at improving the enzymatic hydrolysis and fermentation processes necessary for bioethanol production.

2. Structure of Lignocellulosic Biomass

Lignocellulosic biomass consists of non-fermentable and fermentable sugars, and it contains cellulose (used for hydrolysis processes [27]), hemicellulose, lignin, and silica [28].

Hemicelluloses, the most abundant polysaccharides in nature, are found in the cell wall of agricultural straws. They are connected by hydrogen bonds to cellulose and to lignin by chemical bonds [29,30].

Figure 2 shows the role of pretreatments applied to wheat straw [30]. As can be seen, lignin is one of the three major compounds in biomass lignocellulosic, along with cellulose and hemicellulose, being an amorphous polymer three-dimensional structure consisting of methoxylated phenylpropane structures. In the cell walls in plants, lignin fills the spaces between cellulose and hemicellulose, acting as a resin that holds the lignocellulosic matrix together. Lignin is a secondary product of wheat straw. It is degradable in nature and creates an impermeable barrier in the biomass of wheat straw, connecting cellulose and hemicellulose. Due to the presence of lignin in the wall of wheat straw, they have good durability and resistance to microbial attacks.

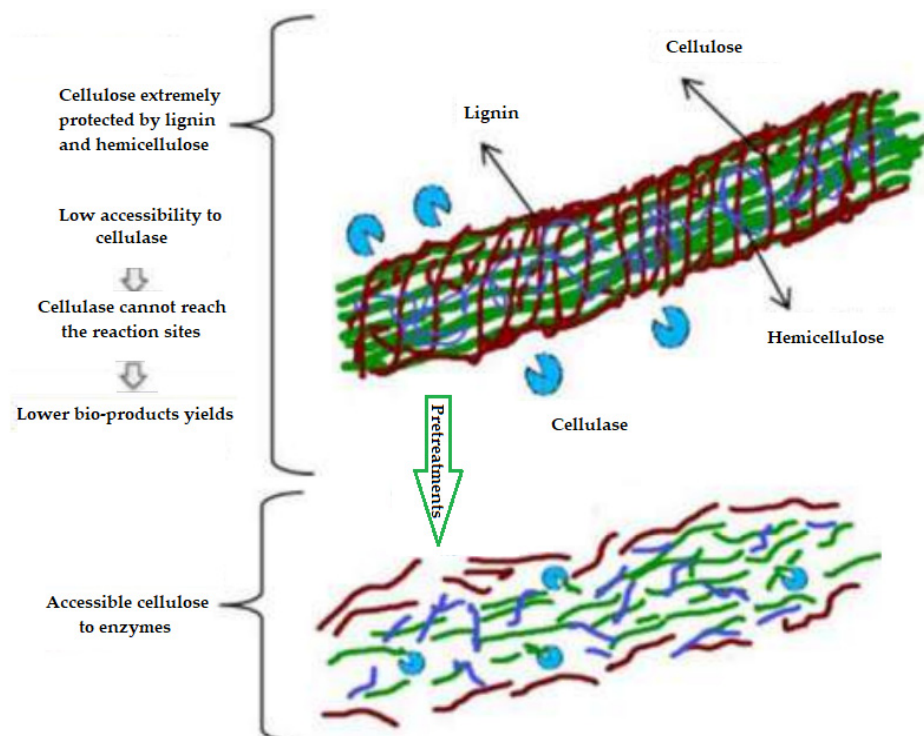


Figure 2. The role of pretreatments applied to wheat straw (adapted from [31]).

Figure 3 shows schematically the process of obtaining bioethanol from pretreated wheat straw, as well as the effect of cellulase on lignocellulosic biomass. Lignocellulosic biomass represents an unlimited and advantageous source of saccharides, including cel-

lulose and hemicellulose (Figure 4). Ethanol is obtained from lignocellulosic materials through cellulolysis (hydrolysis and fermentation). Cellulose is a linear, crystalline homopolymer that is formed by repeating units of glucose joined together by β -D-glycosidic bonds. The structure is rigid, and therefore a rough pretreatment is necessary to break it. Hemicellulose is made up of short, linear and branched chains of sugars. Unlike cellulose, which is a polymer made only of glucose, hemicellulose is a heteropolymer made of D-xylose, D-glucose, D-galactose, D-mannose, and L-arabinose.

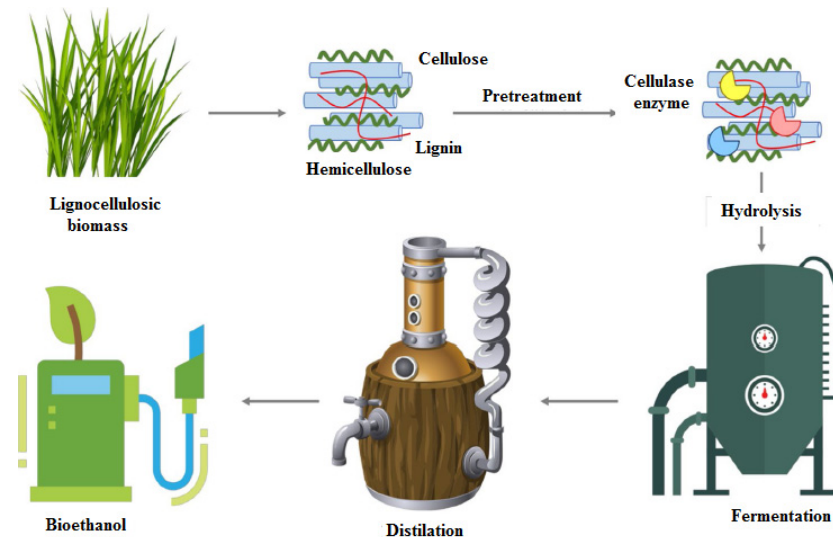


Figure 3. Representation of bioethanol production and the effect of cellulase enzyme on lignocellulosic biomass (adapted from [29]).

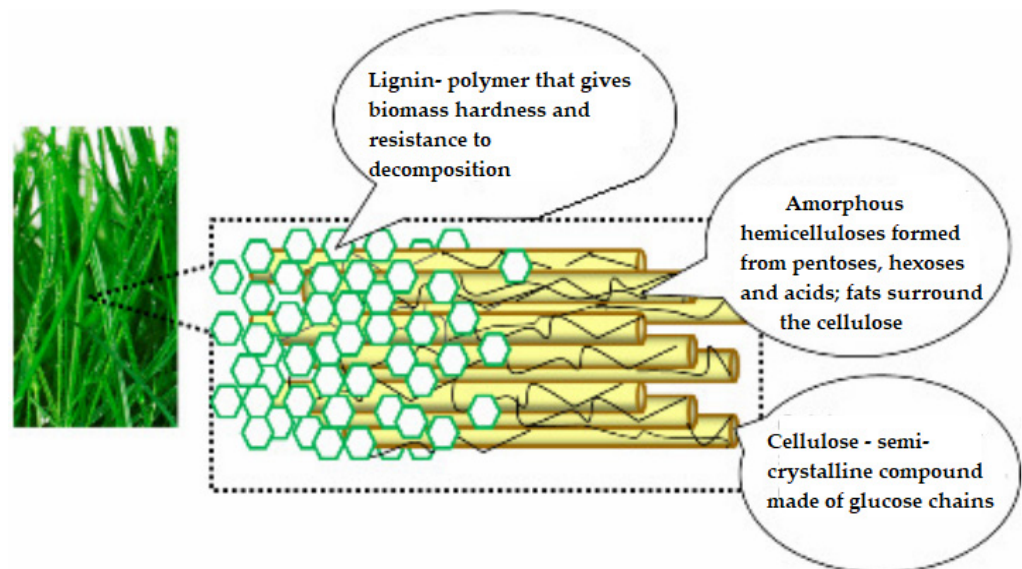


Figure 4. Lignocellulosic biomass (adapted from [29]).

Lignin is present in straw as a structural component, and its content can vary between 10% and 25% of the dry weight. Ash content, consisting of inorganic minerals, can be found in straw, typically ranging from 3% to 10% of the dry weight. Straws may also contain smaller amounts of extracts, proteins, lipids, and other organic compounds, which collectively contribute to the overall composition. It is important to note that these percentages are approximations and may vary depending on several factors, such as plant species, growing conditions and harvesting methods. Lignin is a complex polymer that fills the

spaces between cellulose and hemicellulose in the cell wall. It provides rigidity and hydrophobicity to the biomass. Lignin is composed of phenolic compounds and has a highly branched structure, which makes it difficult to degrade. Heat pretreatment is necessary to further crush the straw to make the cellulose and hemicellulose more accessible to the enzymes in the saccharification process. Due to the heat, pressure, and retention time, the shredded straw is broken and the so-called pre-treated “substrate” is obtained. In the vapor phase, furfural—a byproduct of thermal reactions—is removed from the reactor to a wet scrubber, where the furfural is absorbed into the water. The heat contained in the steam can be recovered and used in other process units [29].

The process of breaking down carbohydrates into simple sugars, most of which can later be easily fermented by microorganisms such as *Saccharomyces cerevisiae*, is called hydrolysis and can be achieved by (thermo)chemical and/or enzymatic pretreatment. Pretreatment is an expensive and decisive stage for the efficiency of subsequent stages in the technological process of obtaining bioethanol. During pretreatment, products can be formed that can inhibit the subsequent enzymatic hydrolysis and/or fermentation processes. The main products that can result from this stage are formic, levulinic and acetic acid, furfural, and hydroxymethylfurfural. Glucose, xylose, arabinose, galactose and mannose are part of the simple sugars that must be obtained by hydrolysis in order for fermentation to occur.

3. Pretreatments Applied to Wheat Straw

Lignin and hemicellulose without pretreatment results in a lower conversion to fermentable sugars of up to 20% of the original cellulose.

According to Tian et al. [31], dry wheat straw contains 30% cellulose, 22–35% hemicellulose, and 17% lignin.

The pretreatments applied to wheat straw to obtain bioethanol are shown in Figure 5: physical, chemical, biological, and physico-chemical.

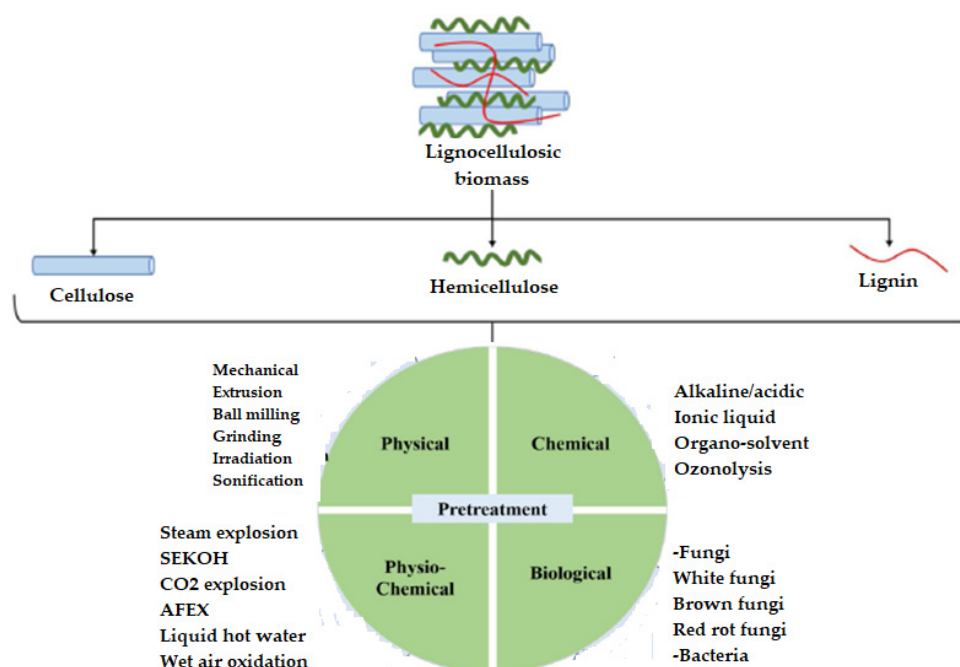


Figure 5. The pretreatments applied to wheat straw to obtain bioethanol (adapted from [29]).

Achieving high fuel efficiency depends on the efficiency of the pretreatment. It is important that the sizes of the biomass particles be reduced and the hemicellulose be dissolved, with these elements being achieved through physical, chemical, and biological pretreatments [31–42].

3.1. Physical Pretreatment

3.1.1. Mechanical Pretreatment

The physical pretreatment processes involve the transformation of the biomass into a fine powder (by shredding, grinding, or chopping) to facilitate subsequent chemical and biological treatments. For example, by chopping, particles of size 10–30 mm are obtained, and by grinding or shredding, particles of approximately 0.2–2 mm are obtained. Depending on the nature of the raw material, the pretreatment method is different, thus minimizing the degradation of the substrate and, at the same time, improving the hydrolysis yield. The better the biomass is shredded, the easier the access of the polysaccharides to the catalytic site of the enzymes becomes. The ideal shredding size varies from a few centimeters to 1–3 mm [43].

Through the mechanical pretreatment of the straws, they are chopped, ground with a hammer mill, balls, a wet disc, or rollers in order to reduce the size of the straws, obtaining an improvement of enzymatic hydrolysis [8,29]. The energy consumed for grinding wheat straw in the hammer mill is $42.57 \pm 2.04 \text{ kWh t}^{-1}$ [8]. The energy consumed by grinding straw depends on moisture, the initial size of the particles, the speed of feeding the material, the properties of the material, and the variables of the machine. It was found that the energy consumption was reduced when grinding wheat straw in the hammer mill to 53.0 kWh t^{-1} from 232.0 kWh t^{-1} [8,32], together with the reduction in their humidity from 19.6% to 9.2% [8].

When the degrees of the hammer and the speed of operation of the hammer mill increased, it was found that the specific energy decreased in the case of grinding wheat straw [8].

Since the flow rate of the material decreased with the decrease in the size of the hammer mill sieve, it was found that the specific energy required for grinding agricultural biomass increased with the decrease in the size of the hammer mill sieve from 30 to 1.6 mm [33].

The specific energy consumption for grinding wheat straw with the sieve mill with 0.8 and 3.2 mm sieves was 51.6 and 11.4 kWh t^{-1} [32]. For sieve sizes of 1.6 mm, the total specific energy consumed for grinding wheat straw was double the case of the sieve of 3.2 mm [8].

Through mechanical or physical pretreatment, the size of the lignocellulosic biomass was reduced to 10–30 mm [31].

Through physical pretreatment, the biomass was heated to a temperature of 50–240 °C [33]. Wheat straw pretreated at 180 °C had a 53% higher yield compared to untreated materials, and the chemical bonds of the lignocellulosic structure of wheat straw were modified [35–39]. The significant elimination of lignin was achieved by thermally assisted alkaline pretreatment of the straws [40]. By ball-milling wheat straw at 80 °C for 30 min, water absorption at 400% (*w/w*) increased the glucose yield by up to 66.69% than at 100 °C; thus, the intake of water during the grinding process made the process efficient [29].

3.1.2. Irradiation of Wheat Straw

Pretreatment of wheat straw by irradiation accelerates the enzymatic hydrolysis of the straw [40]. Electron beam accelerator gamma irradiation of wheat straw increases acid hydrolysis of the straw, while the increasing radiation dose results in sugar reduction yields that are higher compared to non-irradiated straw [41].

The most-used alkaline solution for the pretreatment of wheat straw is sodium hydroxide; thus, by using NaOH/H₂O₂ for pretreatment at a temperature of 50 °C, 3–15 h, a sugar reduction of 61.9 g/L was obtained, the delignification rate was 60%, and the yield of bioethanol was 31.1 g/L, for fermentation condition 37 °C and 96 h.

According to research carried out by Rezanian [40], from wheat straw irradiated with ultrasound and pretreated with alkali 0.2% H₂O₂, for 12 h, hemicellulose was extracted at a percentage of 27.1–28.1% [35].

Through microwave gamma irradiation, a reduction in the oligosaccharide content from 0.04% to 26.78% and glucose from 0.01% to 0.65% was obtained, while the lignin-hemicellulose matrix was decomposed by the sudden increase in temperature [35].

With ultrasound, the lignin was reduced to 85%, while the crystallinity index and the porosity of the biomass surface increased. The bioethanol yield also increased up to 65.8 mg/L, by increasing the sonication time from 5 to 10 min [41].

3.1.3. Pretreatment of Wheat Straw by Extrusion

The extrusion treatment can be performed with an extruder with one or two gears. For the efficient recovery of sugar from wheat straw with high solid lignocellulose, through removing the amorphous region, the crystallinity index is increased by up to 50% [38]. Through the alkaline pretreatment of wheat straw in a reactor with two gears, the amorphous regions were eliminated through the degradation of lignin, leading to the improvement of enzymatic digestibility [44]. Extraction followed by mechanical extrusion was a feasible pretreatment strategy for bioethanol production.

Through this pretreatment, 64.51% of lignin was removed and the cellulose peaks were sharper, increasing the glucan content from 40.83% to 63.16% [29].

Through the extrusion pretreatment, the material is mixed, heated and sheared, causing chemical and physical changes [44–49]. Through this pretreatment, the yield of sugar production from extruded materials was improved, increased hydrolysis efficiency was obtained [50].

3.2. Chemical Pretreatments Applied to Wheat Straw

Through chemical pretreatment of straw with sulfuric acid, the hemicellulose is removed and the decomposition process of the hemicellulosic sugar is accelerated [8].

The chemical pretreatment methods applied to wheat straw are presented in Table 1. It can be observed that the highest glucose yield was obtained by alkaline pretreatment of wheat straw.

Table 1. Chemical pretreatment methods applied to wheat straw (data from [31,33,34]).

Methods	Chemical Reagent	Pretreatment Effect	R
Ionic liquid pretreatment	[BMiM] MeSO ₄ -H ₂ SO ₄ [emim] [CH ₃ COO]	Cellulose digestibility 77%, Glucose yield 76%	[31]
Acid pretreatment	Oxalic acid dihydrate, dilute sulfuric acid 2% H ₂ SO ₄	Total reducing sugar 42%, glucose yield 90%	[31]
Alkaline pretreatment	Cold alkaline (aqueous ammonia 10% NaOH	Glucose yield 93.1%, Lignin removals 59.1%, Xylan digestibility 88%, Glucose yield 73.8%	[33]
Organic solvent pretreatment	5–10% Formic acid acid-free organosolv glycerol organosolv	Glucose yield 40% Theoretical ethanol production yield of 96% Lignin removals 65%	[34]

R-references.

3.2.1. Alkaline Pretreatment

Through alkaline pretreatment with solutions, such as lime, ammonium hydroxide, sulphite, sodium hydroxide, and hydrogen peroxide, lignin is selectively removed without losing sugar and carbohydrate reduction, while biomass porosity and surface area are increased and enzymatic hydrolysis is improved [51]. Alkaline pretreatment methods are, in general, more effective, as a large part of the lignin is solubilized.

The major advantages of this type of pretreatment are that the reactivity of the cellulose increases, a small amount of sugar is degraded, and the costs for raw materials are much lower compared to acid hydrolysis.

By alkaline pre-extraction, the enzymatic hydrolysis of wheat straw was improved [51–53]. The removal of silica at different times and concentrations was carried out using the alkaline reagents Na_2CO_3 and NaOH .

The highest biomass yield was obtained for the treatment with Na_2CO_3 compared to the alkaline pretreatment with NaOH . By treating the straw for 6 h at an alkaline concentration of 0.25 mol/L, the biomass yields were 91.1% and 86.3% for the pretreatments with Na_2CO_3 and NaOH , respectively, because Na_2CO_3 can dissociate less hydroxide ions than NaOH . The extraction of hemicellulose increased with the increase in the pH value and the pretreatment time of the wheat straw with NaOH .

By alkaline pretreatment of wheat straw, silica was removed, leading to the reduction in its negative effect during enzymatic hydrolysis [42,54].

Table 2 shows the production of bioethanol obtained by alkaline pretreatment [39,51]. It can be observed that the best results were obtained by pre-treating the wheat straw with the alkaline Na_2CO_3 pretreatment (11%), while a glucose reduction yield of 85.7% was obtained, lignin was removed in 70.4%, and the yield production of ethanol at 65 (g/L).

Table 2. Obtaining bioethanol by alkaline pretreatment of wheat straw (data from [51,53]).

Raw Material	Alkaline Type	Pretreatment Condition	Reducing Sugars	Delignification Rate (%)	Fermentation Condition	Bioethanol Yield (g/L)	R
Wheat straw	Na_2CO_3 (11%)	75 °C; 10–85 min	Xylose: 85.7%	70.4	30 °C; 96 h	65	[51]
Wheat straw	$\text{NaOH}/\text{H}_2\text{O}_2$	50 °C, 3–15 h	61.9 g/L	60	37 °C; 96 h	31.1	[53]

R-references.

By pretreating wheat straw with hydrogen peroxide, 98% of silicon was removed, and hemicellulose was removed with increased pretreatment time [54].

3.2.2. Pretreatment with Organic Solvent

By pre-treating the biomass with organic solvents, the lignin is removed, the hemicellulose is solubilized, and some organic solvents can be recirculated [25,31,54–56].

Table 3 shows the results of obtaining bioethanol for treating wheat straw with organic solvents. It can be observed that delignification is most efficient in the case of pretreatment with organic solvents.

Table 3. Obtaining bioethanol by pretreatment of wheat straw with organic solvent.

Raw Material	Pretreatment Type	Pretreatment Condition	Reducing Sugars	Delignification Rate (%)	Fermentation Condition	Bioethanol Yield [g/L]	R
Wheat straw	Organosolv	190 °C, 1 h	Glucose: 99	84.5	50 °C; 72 h.	NA	[51]
Wheat straw	Eutectic solvents	70 °C, 9 h	Glucose: 79.7	71.4	50 °C; 72 h	89.8%	[53]

NA: not available. R-references

3.2.3. Pretreatment with Acid

By pre-treating wheat straw with acid, the degradation of hemicellulose is monitored. The following acids are used: acetic, sulfuric, phosphoric acid [57–67].

Table 4 shows the results of bioethanol production obtained from wheat straw treated with sulfuric acid and sodium sulphite [40].

Table 4. Obtaining bioethanol by acid pretreatment of wheat straw (data from [38]).

Raw Material	Acid Type	Pretreatment Condition	Reducing Sugars	Delignification Rate (%)	Fermentation Condition	Bioethanol Yield [g/L]	R
Wheat straw	H ₂ SO ₄ (2%)	180 °C; 10 min	43 g/L	NA	30 °C; 72 h	0.44	[40]
Wheat straw	H ₂ SO ₄ and Na ₂ SO ₃	180 °C; 30 min	NA	21	48 h	17.25 g/g	[40]

NA: not available.

3.2.4. Ionic Liquid Pretreatment

By pretreating wheat straw with acidic ionic liquids, a high yield of carbohydrates and sugars was obtained, enzymatic delignification was improved by maintaining the activity and stability of cellulase, while ether bonds were broken to extract lignin, as they have an effect on lignin depolymerization [68–71]. Sugars were reduced by 80% in the case of wheat straw treated with ionic liquid compared to untreated ones [71]. The following substances are used in this pretreatment: pyrrolidinium-based, imidazolium-based, ammonium-based, phosphonium-based, sulfonium-based, 1-ethyl-3-methylimidazolium acetate [70–72].

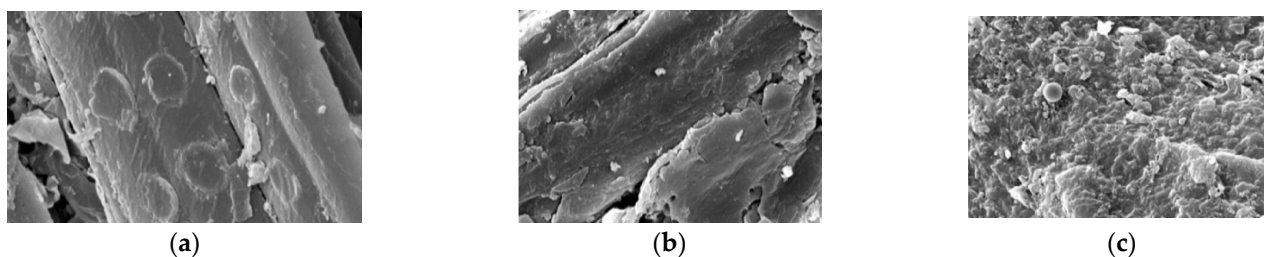
The ionic liquid is a good solvent. It is a salt that melts at room temperature; it is non-volatile; difficult to oxidize; it can replace volatile organic solvents; it accelerates enzymatic hydrolysis; it can be recycled [31,40,65].

One of the main advantages of using ionic liquids in the biomass conversion process is their ability to dissolve a large amount of cellulose and lignin, and the low volatility allows the reaction to take place at high temperatures [64].

The biomass of wheat straw pretreated for 0.5 h and 3 h decreased, being 27.6 and 56.96%, respectively [40].

Untreated wheat straws had a higher content of hemicellulose and lignin compared to the treated ones [40]. The hemicellulose was reduced by 64.45% and 18.6% and the total delignification of the biomass pretreated for 3 hours and 0.5 hours was obtained in the proportion of 80.16% and 45.37% respectively [40]. The pretreatment with ionic liquid favored the disintegration of the amorphous fractions of lignin and hemicellulose from the sample matrix [67].

The morphological aspect of the samples was treated with ionic liquid for 5 h (Figure 6b) and 3 h (Figure 6c) and untreated (Figure 6a) at 3000× magnification, as highlighted by SEM microscopy (Figure 6). It can be observed that, in the case of untreated wheat straw, the surface is orderly, rigid and smooth, while in the treated ones it is rough, agglomerated, and disordered, with large pores and cracks due to the elimination of lignin and hemicellulose from the wheat straw biomass that disturbed the matrix [67].

**Figure 6.** Electron micrographs of wheat straw untreated (a), treated for 0.5 h (b) and treated for 3 h (c), at 3000× magnification (adapted from [68]).

Glucose saccharification production and xylose yields were higher the longer the pretreatment time of wheat straw with ionic liquid [40].

The ethanol yield was higher in the case of using straw treated for a longer time, namely 3 h, compared to wheat straw pretreated for 0.5 h (these being 84.34% and 52.84%, respectively). In the case of untreated biomass from the maximum theoretical yield, the ethanol yield was only 10.76% [40].

The ethanol yield was higher when using wheat straw pretreated for 3 h compared to using wheat straw pretreated for 0.5 h, being 84.34% and 52.84% of the theoretical maximum yield, while only 10.76% was the ethanol yield from the untreated wheat straw [40].

Pretreatment of wheat straw with ionic liquid before enzymatic hydrolysis determined obtaining a higher yield of ethanol due to successful delignification.

3.3. Physico-Chemical Pretreatment

3.3.1. Hydrothermal Pretreatment of Lignocellulosic Biomass

Through this method, lignocellulosic biomass is degraded by using hot water at temperatures between 160 °C and 240 °C [72].

The hydrothermal pretreatment of wheat straw is a physico-chemical treatment that is carried out without reagents [68,73–89]. With this pretreatment, a hemicellulose removal efficiency of up to 97% was observed, and a part of lignin was obtained through their degradation in soluble [68].

Through the hydrothermal pretreatment of wheat straw, a 23.52% reduction in lignin was obtained, while sugars were reduced by 84.15%.

Physico-chemical pretreatment processes include CO₂ explosion, ammonium fiber explosion, steam explosion, humid air oxidation, and hot water processes, which follow wheat straw delignification, sugar reduction, and extraction of hemicellulose from lignocellulosic biomass. The processes that take place during the physico-chemical pretreatment at different temperatures and pressures, as well as the sugar reduction yield, are illustrated in Table 5. It can be seen that the highest sugar reduction was obtained by the CO₂ explosion at a temperature of 190 °C and the pressure of 20–60 bars.

Table 5. Physicochemical pretreatment of wheat straw for the production of bioethanol [58].

Types	Temperature (T) and Pressure (P)	%Yield of Sugar	Advantage	Disadvantage
Wet air oxidation	T: 170–200 °C P: 10–20 MPa	67% Cellulose content, 89% lignin removal,	Simple method suitable for lignin-enriched biomass residue	High cost to maintain it, cellulose is less affected
AFEX process	T: 60–100 °C P: 1.7–201 MPa 27% (<i>w/w</i>) ammonia concentration	42% lignin reduction	Reduce crystallinity and amorphous structure of cellulose	High energy is required to maintain process temperature -Generate toxically compounds—Disturb the sustainability of enzymes
Steam explosion	T: 180–280 °C P: 2.5–7 MPa	Glucose recovery 57–63%	Simple biomass pretreatment	Not relevant for biomass with less moisture amount
CO ₂ explosion	T: 190 °C 20–60 bar CO ₂ pressure	Glucose yields 80.7%	Cheaper Higher yield Low-temperature requirement Simple process Low capital Low maintenance costs Non-corrosion problem High sugar yields	Large amounts of energy are required due to high water consumption
Liquid hot water	T: 160–240 °C P: >5 MPa	Glucose recovery 73.1%		

Ammonia fiber expansion-AFEX.

3.3.2. Pretreatment of Wheat Straw by Steam Explosion

Wheat straw biomass is heated with saturated steam at high pressures for a short period (one minute), followed by the sudden release of pressure causing the steam to expand in the lignocellulosic material, causing the detachment of individual fibers by disrupting the cell wall structure and solubilizing the hemicellulose and lignin [58].

This pretreatment is carried out at temperatures of 160–260 °C, residence times of 15, 30 and 60 min, and a pressure of 689 kPa, followed by sudden depressurization.

Using 0.25% (*w/w*) sulfuric acid in the steam explosion, with a temperature of 121 °C, pressure at 103 kPa, and a time of 60 min, a reduction in the cellulose content of the wheat straw biomass of 34.08% was obtained [69].

3.4. Biological Pretreatment of Wheat Straw

The biological pretreatment of wheat straw to obtain bioethanol is carried out with the help of bacteria, microorganisms (*Aspergillus niger*, *Streptomyces* sp., *Phanerochaete chrysosporium*, *Clostridium* sp., *Trichoderma viride*, *Cellulomonas* sp., *Thermomonospora* sp., *Bacillus* sp., *Trichoderma reesei*), and mushrooms (*Trametes* sp., *Pleurotus* sp., *Pleurotus floride*), which also factor into ecological pretreatment [62–68].

Bacteria and fungi degrade lignin with the help of ligninolytic and hydrolytic enzymes, lignin peroxidase, laccase, and manganese peroxidase [76,77].

A greater degradation of lignin was observed using the bacteria *Sphingobium* sp. SYK-6, *Rhodococcus* sp., *Ceriporiopsis* sp., *Pandora* sp., *galactomyces* sp., and *Mycobacterium* sp. in the biological pretreatment of wheat straw. They release lignolytic and xylanolytic enzymes for the production of bioethanol [79].

Hemicellulose and cellulose are hydrolyzed into monomeric sugars by the use of hemicellulolytic and cellulolytic microorganisms [87].

Biological pretreatment has some benefits, such as low processing costs, chemical recycling after pretreatment, and low energy consumption. The main disadvantage is the low rate of hydrolysis [36]. Fungi and bacteria can generate hydrolytic and oxidative enzymes that can destroy the rigid structure of lignocellulosic biomass. Degradation of cellulose and hemicellulose can be achieved by anaerobes (*Clostridia*) [88].

An improvement of the methane yield by more than 100% was obtained through the enzymatic pretreatment [69,89]. Bacterial and enzymatic pretreatments can be completed in a few hours compared to those with mushrooms, which take a longer incubation time (weeks or months). Through the fungal pretreatment of wheat straw, an improvement of cellulose degradation of up to 80% was obtained [90], the enzymatic digestibility was improved by increasing the yield of xylose and glucose [91], and the degradation of lignin increased [92]. After ten weeks of pretreatment with the *Ceriporiopsis subvermispora* strain, an increase of up to 60% in biomass digestibility and an increase of up to 44% in sugar yield were obtained [40].

After pre-treating wheat straw with white-rot fungus *Irpex lacteus* for 20 min at 120 °C, the bioethanol yield was 12.5 g/L, sugar reduction was 11.5%, and the delignification rate was 45.8% [93].

4. Pretreatment Limitations

The lignocellulosic biomass pretreatment methods have certain limits:

- Pretreatment with an organic solvent has a low biomass recovery rate. The optimization of the pretreatment conditions depends on the pretreatment time and temperature, the type of catalysts and the solvent concentration [93];
- During biological pretreatment, lignin derivatives can poison microorganisms.
- To shorten the pretreatment time and improve enzymatic digestibility, fungal pretreatment combined with other pretreatments is recommended [40,94];
- Microwave irradiation implies a high energy demand, high cost of pretreatment, and a lack of large-scale equipment. The design and expansion of more energetically efficient microwave pretreatment reactors is recommended [95,96];
- In pretreatment with ionic liquid, there are no economic solutions for recycling the ionic liquid [40];
- Chemical pretreatment with acid and alkaline implies a requirement of intensive energy, high costs, and harmful by-products [40].

Through chemical, physical or biological methods, the total or partial solubilization of lignin and hemicellulose takes place [97–99].

Pretreatment by chemical methods, in the presence of dilute acids, has the disadvantage of hemicellulosic saccharides breaking down into furans and phenols, compounds that inhibit the fermentation process, thus reducing the yield of ethanol [98].

Chemical methods (with diluted acids, alkaline media, ammonia, organic solvent, sulfur dioxide, and carbon dioxide) are the most used; however, for economic reasons and environmental protection, it is expected that they will be replaced by physical methods [100]. The choice of the type of pretreatment step influences the ethanol yield. Chemical pretreatment methods involve splitting the fibers in various conditions, from highly acidic to alkaline environments. In these conditions, different constituents of the biomass can be affected. For example, acid pretreatment causes the hydrolysis of hemicellulose while the cellulose and lignin fractions remain intact in the solid residue [101,102]. In most cases we work with H_2SO_4 . Pretreatment in alkaline environment affects only lignin [98].

For pretreatment in an alkaline medium, bases such as sodium hydroxide or calcium hydroxide are used. The entire amount of lignin and part of the hemicellulose is removed. An advantage is the increase in cellulose reactivity. The costs for raw materials are much lower compared to acid hydrolysis. However, the use of high concentrations of reagents requires the treatment of wastewater and an increase in costs for the neutralization of the waste. Alkaline pretreatment methods are, in general, more effective, as a large part of the lignin is solubilized but most of the hemicellulose remains in an insoluble state [98].

The use of the process with solvents presents some advantages compared to traditional chemical methods, e.g., it can use small-sized lignocellulosic material, facilitating the removal of impurities; the possibility of isolating and recovering lignin in an unaltered form; and recovery with good yields of saccharides from hemicellulose.

The biological method uses a low amount of energy. The disadvantages of the method include the very low speed of hydrolysis and lignin derivatives poisoning microorganisms. Biological methods of biomass pretreatment can be combined with chemical ones.

Bioethanol contributes to the reduction in CO_2 emissions, being a beneficial fuel for the environment [100]. Using a bioethanol blend as fuel for cars can significantly reduce oil use and greenhouse gas emissions. Cellulosic ethanol can generate a reduction in greenhouse gas emissions of approximately 90%, with carbon dioxide emissions becoming almost equal to zero.

5. Conclusions

Taking into account the fact that wheat straw is waste, most of the time being incinerated, this paper presented the pretreatment methods of wheat straw used as raw material for obtaining bioethanol.

Thus, the mechanical, physical, chemical and biological pretreatments applied to wheat straw to obtain bioethanol were presented. It was observed that the pretreated wheat straw had a higher bioethanol yield compared to the untreated ones. Through the mechanical pretreatment of the straws, improving the enzymatic hydrolysis by reducing the size of the straws was set as a goal.

Physical methods include heating and irradiation, which change the structure and properties of wheat straw.

Chemical pretreatments involve the use of acids, alkalis, and organic solvents to remove lignin and hemicellulose, making the cellulose more accessible for hydrolysis.

Biological pretreatments use microorganisms and fungi to degrade lignin and other complex compounds, enhancing cellulose decomposition.

Formulating an efficient pretreatment strategy for the conversion of lignocellulosic biomass to ethanol is an extremely important step in making the technology commercially feasible.

Formulating an efficient pretreatment strategy for the conversion of lignocellulosic biomass to ethanol is an extremely important step in making the technology commercially feasible.

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