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Treatment of Lignocellulosic Waste for the Production of Bioethanol

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Abstract

Bioethanol produced from renewable biomass, especially lignocellulosic biomass, provides opportunities for sustainable, cleaner, environmentally safe, carbon neutral and green alternatives to fossil fuels. This literature review briefly describes the aspects related to bioethanol production and focuses on theoretical approaches for process improvement and improving the efficiency of bioethanol production from lignocellulosic biomass. A systematic review of previous literature is conducted. Known data sources are consulted and relevant research is filtered through certain keywords. Although lignocellulosic waste is present in massive quantities on planet earth, it is not properly utilized for bioethanol production due to many obstacles in the bioconversion process, such as pretreatment, high cost of enzymes, conversion of mixed sugars, fermentation and distillation. Studies show that high grade bioethanol is obtained by saccharification, fermentation and stratified distillation. The production of bioethanol from lignocellulosic waste offers the advantage of generating a renewable and less polluting source of energy than fossil fuels. Different treatments and processes have been developed to generate a production of bioethanol that has a higher yield with low costs with the aim of increasing the availability of this energy source to the general public. Lignocellulosic ethanol is not yet competitive enough and it is necessary to improve several parameters such as primary treatment, microorganisms for fermentation and distillation to obtain a high purity product.

Keywords: *cellulosic wastes, microorganisms, lignocellulosic.*

Introduction

Fossil fuel is one of the non-renewable resources, as well as one of the main contributors to the emission of greenhouse gases, the excessive consumption of fossil fuel at present is the main reason for the global energy crisis and the deterioration of the climate (Rezania *et al.,* 2020). The global rate of oil consumption is estimated to increase from 21 to 60 percent by 2030 and will be completely depleted between 2069 and 2088.(Maity & Mallick, 2020)

Bioethanol is the largest contributor of renewable energy globally, in 2019 the production of this biofuel reached 110,000 million, the US and Brazil produce 94 billion L of bioethanol per year, with the main producers around 85% globally (Dong *et al.,* 2018). Ethanol can be blended with gasoline in different proportions at 10% (E10) covering most of the international demand (Susmozas *et al.,* 2020).

Biofuels can be defined as a renewable and non-toxic energy source that is derived from biological materials such as plants and microbes through a biochemical process, i.e. fermentation by microorganisms. Second-generation bioethanol is obtained from the complete plant structure of lignocellulosic materials.(Maity & Mallick, 2020)(Shahzad & Wu, 2019). Bioethanol produced from lignocellulosic materials is shown as an alternative that does not affect the availability of edible

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products, this biotransformation process is emerging as a potentially sustainable energy resource (Deshavath *et al.,* 2019). Among the components of biomass, lignocellulose is the most abundant with a production of 170 billion metric tons per year (Su *et al.,* 2020) Corn, wheat and sugarcane are the most used for bioenergy conversion has different percentages of cellulose, hemicellulose and lignin, as for cellulose corn stalks have 37%, wheat straw 32.9% and sugar bagasse 40.0%, hemicellulose 16.8%, 24% and 27%, respectively (Miskat *et al.*, 2020).

The process of obtaining bioethanol mainly comprises a pretreatment followed by the hydrolysis of the lignocellulosic structure of the biomass to obtain fermentable sugars, fermentation and finally the distillation of the fermented product (Albarracín *et al.,* 2015). Distillation is the final step of bioethanol production, and the purpose of distillation is to separate and purify the bioethanol from the fermentation broth (Xin *et al.,* 2017). This research aims to study the process of lignocellulosic waste treatments for the production of bioethanol.

1.1. Lignocellulosic residues
Lignocellulose is the most abundant and renewable material in the world, it is composed of cellulose, hemicellulose and lignin, whose proportions in plants vary as follows: 20-55% cellulose, 16-85% hemicellulose and 15-40% lignin (Cai *et al.*, 2017). Lignocellulosic biomass feedstocks available for energy purposes come mainly from the agriculture, forestry and industrial sectors. Agricultural wastes and forest residues are the most promising biomass feedstocks because of their abundance and relatively low cost. (Collard & Blin, 2014)

1.2. Cellulose
Cellulose is a natural homopolysaccharide consisting of D-glucose units, linked by β-1,4-D-glycosidic bonds, forming a linear polymer that presents a structural order, in which its hydroxyl groups generate strong intramolecular bonds acquiring crystalline properties (González *et al.*, 2017). Cellulose represents about a third of the composition and is biosynthesized in the process of plant photosynthesis, producing a large amount of cellulose annually in the world (López *et al.*, 2018).

1.3. Hemicellulose
It is a polymer constructed by sugar units such as cellulose, but unlike cellulose, the main chain of hemicellulose consists of pentoses. This homopolymer or heteropolymer possesses short branches linked by bonds β (1,4) glycosidic and occasionally β (1,3) glycosidic. Hemicelluloses are easily hydrolyzable because their structure is amorphous and hydrophilic, the polymers that make it up with hexoses, pentoses and uronic acids (Apaza & Ramirez, 2021)(Qaseem *et al.,* 2021).

1.4. Lignin
It is another biopolymer abundant in nature and that shows a remarkable divergence compared to other macromolecules that make up the cell wall of plant cells, it is amorphous, branched, heterogeneous and hydrophobic (Torres *et al.,* 2019). Lignin surrounds the microfibrils of cellulose and hemicellulose, it is linked to the latter by certain strong bonds of covalent type, there are different types of lignin, depending on the plant species of origin, and which differ from each other by the aromatic rings of the monomers (Llenque *et al.,* 2020). The physical properties of lignocellulosic biomass include particle size, density, fluidity, crushability, moisture sorption, and thermal properties (Cai et al., 2017).

Board 1. Chemical composition of different lignocellulosic materials

Lignocellulosic materials	**Cellulose %**	**Hemicelulosa %**	**Lignin %**
Hardwood stem	40-55	24–40	18–25
Softwood stem	45–50	25–35	25–35
Nut shell	25–30	25–30	30–40
Corn cob	45	35	15
Grass	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat straw	30	50	15
Leaf	15–20	80–85	0
Cottonseed hairs	80–95	5–20	0
Newsprint	40–55	25–40	18–30
Chemical pulp waste documents	60–70	10–20	5–10
Primary wastewater solids	8–15		24–29
Pig waste	6	28	-
Cattle manure solids	1.6–4.7	1.4–3.3	2.7–5.7
Meal Bermuda	25	35.7	6.4
Cane bagasse	45	20	
Change grass	45	31.4	12

Fountain. *Edited from* Zumarraga, (2012)

1.5. Uses of lignocellulose

Lignocellulosic biomass is an important source of renewable energy with potential in the production of biofuels, cogeneration of electrical energy and generation of chemical compounds, among other applications.(Peña & López, 2020). Due to its unique structure and properties, cellulose is one of the most common and widely used polymers in the food packaging industry (Liu *et al.,* 2021). In addition, lignocellulose is used for biodegradable plastics and for papermaking (Yaradoddi *et al.,* 2020).

1.6. Lignocelluloses for bioethanol production

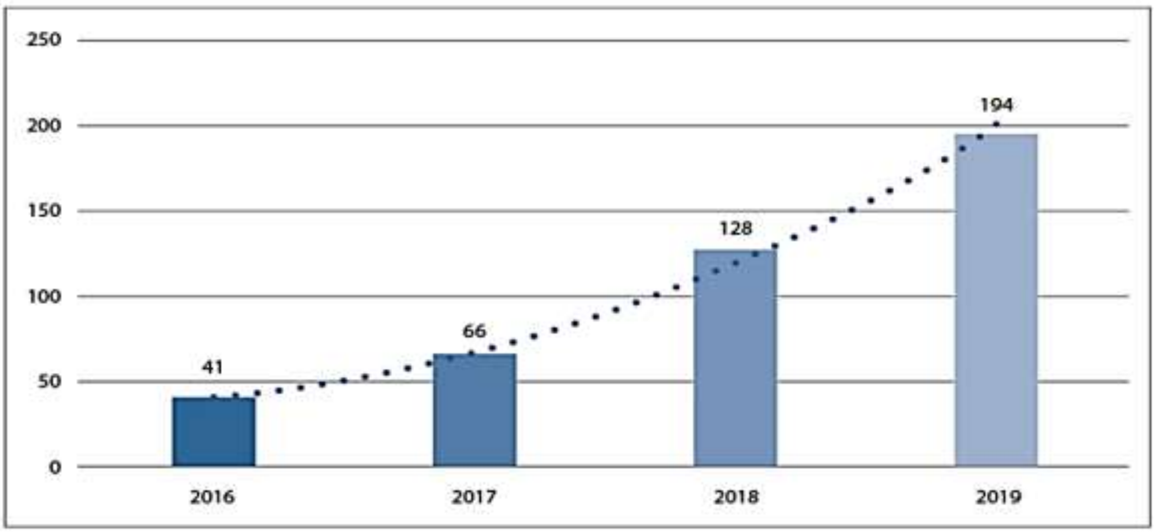
Biofuels produced from lignocellulosic feedstock by microbial fermentation and saccharification are called the second generation of biofuels (Rezania *et al.,* 2020). Lignocellulosics are processed for bioethanol production through three main operations: pretreatment for delignification is necessary to release the cellulose and hemicellulose prior to hydrolysis to produce fermentable sugars including glucose, xylose, arabinose, galactose, mannose and fermentation of reducing sugars.(Mohanty & Abdullahi, 2016)

Bioenergy is one of the renewable energy sources that can gradually replace the use of fossil fuels, bioenergy contributes to the reduction of greenhouse gas emissions (Bañuelos *et al.,* 2018).

1.7. Biothanol production in Ecuador

In 2010, in the province of Guayas, the Eco país pilot plan was initiated with the purpose of testing the E5 fuel mixture, composed of 5% (v / v) of bioethanol and 95% of gasoline, which was analyzed in 2014. And(Paredes, 2015)n 2016, it was proposed to extend the use of E5 to the entire country and, subsequently, to increase to 10 and 15% the percentage of bioethanol in the mixture, in pursuit of the total replacement of the demand for extra type gasoline for the year 2019 (Follow *et al.,* 2020).

Figures 1. *Projection of bioethanol production in Ecuador*



Source: Sigüencia et al., (2020)

1.8. Process of transformation of lignocellulose residue to bioethanol

Bioethanol: It is a biofuel generated through the fermentation process of organic compounds containing sugars, cellulose goes through an enzymatic decomposition process and is transformed into fermentable sugar to generate bioethanol (Monroy et al., 2017). Characteristics: This organic chemical is a toxic, colorless, odorless, molecular weight 32.04 liquid with a boiling point of 64.7 °C, volatile and flammable.(Muhaji & Sutjahjo, 2018)

Bioethanol is a promising substitute for fossil fuels to alleviate the energy crisis, bioethanol is an alternative energy, they have been developed and attract much attention for their renewable characteristics since they are obtained from lignocellulosic biomass (Chen et al., 2021). The following process diagram details the processes of transformation of lignocellulosic biomass to bioethanol.

Figures 2. *Process of transformation of lignocellulosic residue to bioethanol*

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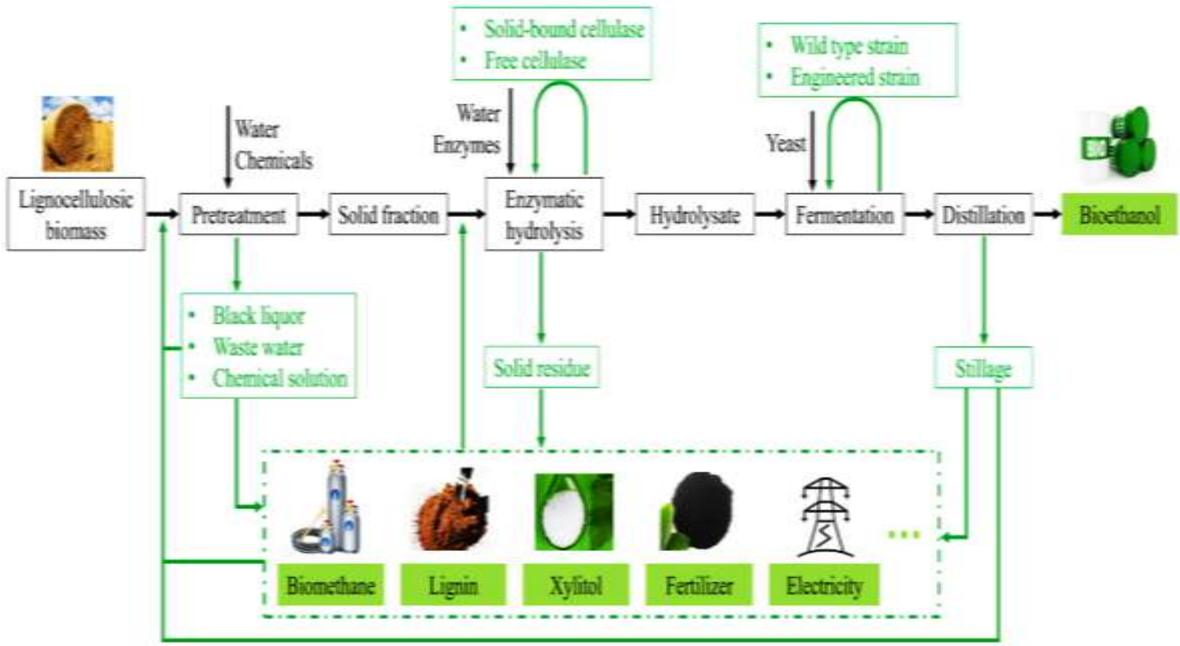

Source: Chen et al., (2021)

a.Pretreatment

Physical pretreatment: It consists of the reduction of particle size between 10 to 30 mm and 0.2 to 2 mm by crushing, which increases the surface area of lignocellulosic materials. Reducing the size may give better results, but a very fine particle size can have negative effects on downstream processes, such as enzymatic hydrolysis. (Kumari & Singh, 2018)(Mohanty & Abdullahi, 2016) Chemical pretreatment: It is a crucial step of bioethanol production, improves available cellulose and is accessible to enzymes, acid solubilizes polysaccharides especially hemicellulose into monomers by enzymatic hydrolysis leading to improved biofuel production (Fakayode et al., 2021).

Enzymatic hydrolysis: It is applied in lignocellulosic biomass by enzyme called cellulose, amyloglucosidase and amylases that help degrade sugars such as hemicellulose, cellulose and lignin into monosaccharides such as glucose, fructose, galactose, under controlled pH conditions. The solid and liquor are the main results after pretreatment, the solid is rich in cellulose which is the main material for the next steps, while the liquor is the waste that is drained. (Martinez, 2018)(Zhou et al., 2019)

Figures 3. *Pretreatment of lignocellulosic biomass*

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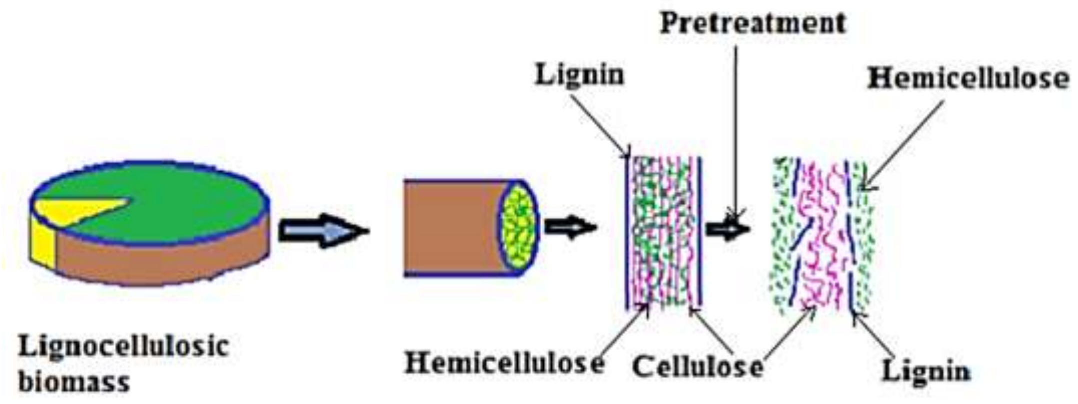

Fountain: Kumari & Singh, (2018)

b.Fermentation

After hydrolysis generates fermentable sugars, these carbohydrate monomers C-6 and C-5 can then be fermented to ethanol by bacteria and yeasts that have been modified to ferment both hexose and pentose sugars. Among the large number of bacteria and yeasts capable of fermenting these sugars is the (Mikulski & Kłosowski, 2020)Saccharomyces cerevisiae and Zymomonas mobilis are the two species currently used on an industrial scale for the production of bioethanol (Its et al., 2020).

The typical fermentation temperature and fermentation time for bioethanol production are about 25-30 °C and 6-72 h (Gavahian et al., 2019). Submerged fermentation: This method involves the cultivation of microorganisms in the broth of liquid medium for the production of the desired product, the microorganism breaks down the nutrients and the desired product is released into the broth, in this type of fermentation, the nutrient is consumed quickly, so it is necessary to add nutrients continuously, the mode of operation can be batch or continuous (Devi et al., 2021).

Fermentation in solid state: The microbial culture on the substrate that is insoluble, also provides surface and nutrients for growth without the presence of liquid medium, the low amount of moisture limits the number of microorganisms, the consumption of nutrients is slow and constant provides a high concentration of enzyme, the mode of operation is mainly batch (Hamdi et al., 2014).

Board 1. *Some microorganisms used in the production of bioethanol*

Microorganism	Biomass
Pichia stipites NRRLY-7124	Coffee beans, hazelnut shell
Escherichia coli FBR5	Wheat residue.
Saccharomyces cerevisiae	Used coffee beans, cassava starch, sorghum residue
Trametes hirsuta	Rice residue
Schizosaccharomyces pombe	Sugarcane bagasse
Pachysolen tannophilus	Sugarcane bagasse

Fountain: Edited from Montfort (2018)

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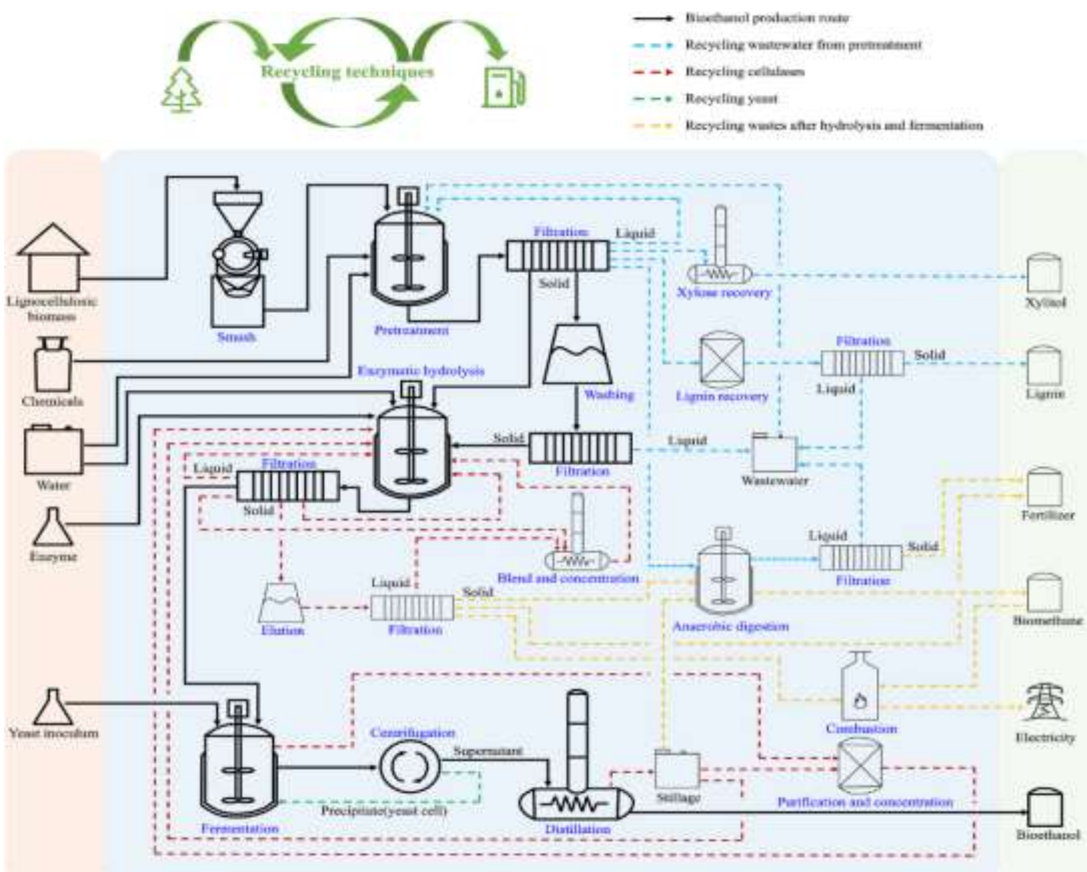
c.Distillation:

Once the fermentation stage is finished, the ethanol is recovered by distilling the fermented broth, however, conventional distillation concentrates the ethanol to its azeotropic point with 95% water, which is also known as "hydro" or "hydrated" ethanol, the continuous dehydration of azeotropic ethanol produces 99.6% ethanol "anhydrous" alcohol (Gavahian et al., 2019).

Oscillating distillation: Pressure oscillation distillation takes advantage of the characteristic that the composition of the azeotrope has a significant change with pressure to achieve separation, so it is only applicable to the azeotropic mixture that is sensitive to pressure (Liang et al., 2017).

Azeotropic distillation: Mixtures can be separated with the help of a drag filter, however, the azeotropic system also brings some challenges such as multiple stationary states and high energy (Chen et al., 2016). Extractive distillation: It is an important and widely used technique for separating binary or multiple azeotropes in the chemical industry due to the flexible selection of potential dragging agents (Cao et al., 2017).

Figures 4. *Recycling process diagram for lignocellulosic bioethanol production*



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1.9. Bioethanol as a renewable energy source

Bioethanol is mostly efficient and clean, can be used in fuel cell systems has more attractive characteristics for sustainable energy development, can be used as fuel to generate hydrogen and use it in fuel cell systems in the near future (Palanisamy et al., 2021). The following table details the generation of energy from bioethanol.

Board 3. Electricity generation from solid waste after the production of lignocellulosic bioethanol.

Raw material	Bioethanol (kg/t feedstock)	Electricity (kWh/t bioethanol produced)	Equipment for electricity generation
Corn stover	254	5385	Boiler shaft and turbine
Wheat straw	260	4335	Boiler shaft and turbine
Rice straw	215	5981	Boiler shaft and turbine
Sugarcane bagasse	234	5332	Boiler shaft and turbine
Poplar sawdust	236	5166	Boiler shaft and turbine
Rice husk	133	2627	Cogeneration with gas turbine
Plantain	206	1147	
Sugarcane bagasse	114	2912	Combustion with high pressure steam cycling system (using distillation
Sugarcane bagasse	114	4480	Combustion with high pressure steam cycle system (using vacuum distillation)

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Sugarcane bagasse	114	3100	Integrated biomass gasification with combined cycle system (using distillation

Fountain: Edited from Chen et al., (2021)

Substitution of bioethanol for gasoline

Biofuels could be used as substitutes for diesel and gasoline, as fossil fuels have a higher emission rate than biofuels (Miskat et al., 2020). Addiction to alcoholic fuels represents a valid strategy to improve the use of biodiesel in compression ignition engines, due to the low density and viscosity of alcohol, mixtures of biodiesel with alcohol overcome some of the drawbacks of pure biodiesel fuel (Caligiuri et al., 2019). E5: 5% bioethanol and 95% gasoline European regulation; E10: 10% bioethanol and 90% gasoline most commonly used in the U.S.; E85: 85% bioethanol and 15% gasoline used in vehicles with special engines: E95 and E100: 95% to 100% bioethanol blend (Cardenas et al., 2021).

RESULTS

The U.S. Department of Energy has given a more advanced comparison by stating that the energy produced by grain-based ethanol especially corn and wheat is 26% more than what is needed for production, while cellulosic ethanol gives 80% more energy.(Shahzad & Wu, 2019) In the research conducted by Bañuelos et al., (2018) resulted in bioethanol of high purity (or at least similar to those of analytical ethanol, 99.8%), from a halophyte plant Salicornia Bigelovii being enzymatic hydrolysis a fundamental factor since it reached an overall glucose yield of 91%. Chen et al., (2021), inflated the yield of bioethanol acquired from different lignocellulosic feedstocks as shown in the table below.

Board 2. *Production of bioethanol and biomethane from lignocellulosic waste*

Raw material	Solid concentration (%)	Ethanol concentration (g/L)	Bioethanol yield (%)	Biomethane yield (ml/g of volatile solids)
Corn stover	24	76	78.30	120
Rice straw	10	17	69.5	99
Hardwood sycamore	10	-	40	75
Coniferous pine	10	-	22.1	45,4
Aquatic weeds	10	15.3–20.4	80.0–90.1	209–257b
Citrus peel residues	-	30.7	-	342
Wheat straw	7.5	-	90	331
Sweet sorghum stalks	5	13,3	80	272.2
Sugarcane bagasse	15	27,2	60	237

On the other hand Deshavath *et al.,* (2019), acquired a conversion efficiency of bioethanol from glucose, xylose and arabinose of 95%, 82% and 55%, respectively from corn stalk, this was thanks to

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the maximization of hydrolysis of hemicellulose and cellulose in monomeric sugars. Similarly Ganguly *et al.,* (2020), conducted a different research in which he extracted bioethanol from lignocellulosic kitchen waste, where the waste was hydrolyzed, in the fermentation process Saccharomyces were used *cerevisiae* and bioethanol production was a maximum of 96%.

CONCLUSION

The production of bioethanol from lignocellulosic waste offers the advantage of generating a renewable and less polluting source of energy than fossil fuels. Different treatments and processes have been developed to generate a production of bioethanol that has a higher yield with low costs with the aim of increasing the availability of this energy source to the general public. The maximum yield for obtaining bioethanol is the hydrolysis process through which it obtains a greater efficiency of reducing sugars for fermentation. The use of renewable and less polluting energy can help us in the constant effort to reduce the greenhouse effect and all negative phenomena.

Lignocellulosic ethanol is not yet competitive enough and it is necessary to improve several parameters such as primary treatment, microorganisms for fermentation and distillation to obtain a high purity product. Bioethanol from these residues can be used for transportation purposes, as it does not require major modifications to engine configuration.

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