Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

A comprehensive review on bioethanol production from corn stover: Worldwide potential, environmental importance, and perspectives

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A B S T R A C T

Corn is the second most abundant crop produced worldwide annually. Its residue, corn stover, is among the three most agricultural residues globally and the first one in the United States. The available corn stover in the world could be used to produce more than 45 million cubic meters of bioethanol (60% of the world production) instead of being mainly burnt on the fields. This practice could potentially reduce Green House Gases (GHGs) emissions by more than 150 million tonnes of CO_2 equivalent per year. A comprehensive review on pretreatment, saccharification and fermentation was performed in this study with investigating the effect of each of these steps on the whole process. The results showed that pretreatment is the most crucial step that hinders bioethanol production from corn stover, whereas newly developed methods like ionic liquids show promising results of 90% lignin degradation. A review on the techno-economic analysis performed in the literature indicated that the integrated biorefinery approach can be employed as an efficient strategy to cut the ethanol minimum selling price to half (0.27 $/L) with an average capital cost of 475 million dollars.

1. Introduction

Annually, about 4.2 million people die because of the polluted ambient air [1]. During the last century, a huge amount of carbon dioxide (CO_2) has been released into the atmosphere. The average global atmospheric CO_2 in 2018 was 407.4 ppm, while it has been reported that the last time that such large amounts of this gas existed in the earth's atmosphere dates back to about 3 million years ago [2]. CO_2 is now considered the main greenhouse gas (GHG) emitted by human activities [3]. If human activities continue as they are, annual greenhouse gas emissions will reach 150 gigatonnes (Gt) of carbon dioxide equivalent, meaning a world more than 4 °C warmer than it is today [4]. This difference is close to the difference between today's world and the last ice age. The result of this temperature rise would be droughts, major floods, heatwaves, and rise of sea levels up to 20% in tropical regions. Moreover, this change will lead to a huge biodiversity loss, with climate change being the major reason for ecosystem shifts [5].

Carbon dioxide released from burning fossil fuels accounts for 65%

of the global CO_2 emissions [3]. The fossil-fuel-based carbon dioxide gets released into the atmosphere with no way of being absorbed again and remains in the atmosphere. The CO_2 taken from the atmosphere by plants over millions of years are getting back to it in a few centuries by burning fossil fuels [2]. The European Commission has recently set a target of reducing the use of fossil fuels by 55% by 2030, compared to 1990 [6].

One of the hopes to reduce CO_2 emissions is the use of biofuels instead of fossil fuels. Global biofuel production increased to 154 billion liters (by 7%) in 2018, and it is predicted that the production capacity will increase by 25% by 2024 [7]. Ethanol is a conventional biofuel and an additive to gasoline. Ethanol also has wide applications in different industries, including perfume, flavoring and essence, and the medical industry [8].

Biofuels are categorized into four generations. First-generation ethanol refers to the ethanol produced from edible sources. Second-generation bioethanol is produced from non-edible feedstocks. Processes involved in third-generation (marine organisms) and fourth-

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generation (genetically improved algae) bioethanol mostly make use of algae. First-generation bioethanol is the most common biofuel produced in the world.

The most common sources of first-generation ethanol are sugarcane and corn, which are used for bioethanol production mostly in Brazil and the United States. First-generation bioethanol production is well commercialized globally, while this production route utilizes large amounts of water, mainly related to crop cultivation. Moreover, with an increasing demand for food, the use of food resources for fuel production has led to increases in the price of first-generation bioethanol. As a case in point, biofuel production has led to a 4% increase in oilseed prices between 2000 and 2010 and a 1–2% increase in cereal prices in the world over the same period [9]. With the critical situation of water and food resources in the world, it is important to turn into more sustainable ways of bioethanol production.

Second-generation bioethanol, which is mainly obtained from lignocellulosic biomass such as crop residues, is more favorable than the former one since it does not compete with human food resources. Corn stover is one of the most available and abundant crop residues that can be used for second-generation biofuel production. Nonetheless, an additional pretreatment step is needed in the process of manufacturing bioethanol from lignocellulosic compounds. This pretreatment may represent a barrier for second-generation bioethanol being economically profitable. The recent technological developments for the bioconversion of corn stover to ethanol have been reviewed by Zhao et al. [10], emphasizing pretreatment technologies. As we move forward in time, more efficient pretreatment methods are being developed to address this issue.

The advanced generations, meaning second, third, and fourth generations, demand more research and investment as they have shown their potential to produce bioethanol sustainably. They can get closer to commerciality with each advancement. The European Commission has set the target to increase the share of advanced biofuels in biofuel production in the transfer sector to 3.5% in 2030 [6].

The main objective of this paper is to review ethanol production from corn stover as a potential feedstock for second-generation bioethanol. This paper commences with fundamental information, processes, and technologies involved and assesses potentials in the world. Ethanol uses and biorefinery approaches are reviewed here. Lastly, the sustainability of the process is evaluated using techno-economic assessments.

2. Ethanol production from corn stover

2.1. Corn stover

Corn (or maize) is a useful crop both for humans and animals [11]. There are four main types of corn: sweet corn, dent corn (or field corn), flint corn (or Indian corn), and popcorn. Dent corn, the most widely grown kind, is used to feed farm animals. Flint corn has a hard shell; therefore, it is used for decoration. Popcorn is a kind of flint corn, but since it has its characteristics (like higher moisture content that leads it to explode when heated), it is categorized into a different group. Sweet corn is an edible-for-human kind of corn, which has higher sugar amounts than the other types [12]. Since sweet corn is valuable to humans, dent corn is the kind that is used for first-generation ethanol

production around the world.

Corn stover refers to husks (8%), cobs (15%), leaves (28%), and stalks (48%) that are left on the farm after harvest [13]. As typical lignocellulose, corn stover is composed of cellulose, hemicellulose, and lignin, forming a complex and recalcitrant structure. The composition of corn stover can vary based on its type. Table 1 shows some of these variations based on location. A study conducted by NREL (National Renewable Energy Laboratory) [14] showed variability in lignin content from 11.5 to 24% of the dry mass of over more than 1000 corn stover samples of 2001 North America. However, corn stover generally consists of 70% cellulose and hemicellulose and 15–20% lignin.

About half of the corn plant is corn stover. It means that the mass ratio of corn stover to corn grain is 1:1 [15]. Corn stover is the most abundant agricultural residue in the United States [16]. A study performed by the U.S. Department of Agriculture and the U.S. Department of Energy in 2005 estimated that by 2030 between 170 and 256 million dry tons of corn stover could be harvested sustainably, which could potentially be used for the manufacture of 54.9–82.5 billion liters of corn-stover-derived bioethanol, equivalent to around 12–18% of the 2020 gasoline use in the United States [16,17].

2.1.1. Cultivation and harvest

Corn cultivation needs large amounts of water, which accounts for 99% of the required water for ethanol production from corn [22]. A high increase in evapotranspiration and decrease in precipitation should, however, co-occur to supply corn water requirements. In an interesting study, Lihua Lv et al. [23] investigated the conventional methods of corn cultivation in two regions of China and tried to optimize them. Although the results were different for the regions, they concluded that under the optimized cultivation, irrigation could be lowered to achieve the same and even higher yields, thus increasing water efficiency [23]. With the critical situation of water resources in the world, it is important to conduct more such studies.

In another study, Sornpoon and Jayasuria [24] put different tillage practices in Thailand under scrutiny and concluded that subsoiler tillage is the best practice when compared to three conventional methods and no-tillage at all. Subsoiler tillage improved soil physical properties and corn production (with a grain yield of 35–216% higher than the other four methods) [24].

The mean daily temperature is an important factor affecting the number of days for this crop to mature. Corn is able to grow in temperatures ranging from 1.5 to 45 °C, with the optimum temperature being around 18–20 °C. To express the reverse relationship between the temperature and the growth rate, the sum of mean daily temperatures is reported for corn stover. For instance, 2500 to 3000°-days are needed for corn to reach its medium age.

The amount of salt in the soil should be controlled as well since it is an important factor for corn growth [11].

Corn grain is considered the main product of corn cultivation and irrigation, while stover that makes up about half of the corn plant can be deemed an important byproduct. Therefore, the partitioning ratio of corn stover in material and energy requirements as well as environmental impacts is less than that of corn. Based on economic values and mass/energy contents, the partitioning ratio of corn stover was estimated to be 11.8 and 37.5%, respectively [25].

Table 1
Corn stover compositions reported in different studies.

Location	Glucan (%)	Xylan (%)	Arabinan (%)	Galactan (%)	Lignin (%)	Ash (%)	Other (%)	Reference
Ohio, U.S.	38.42	18.52	2.82	1.60	20.18	3.82	14.64	[18]
Italy	36.8	22.2	5.5	2.9	21.2	6.5	4.9	[19]
Colorado, U.S.	36.1	21.4	3.5	2.5	17.2	7.1	12.2	[19]
Nebraska, U.S.	32.4	19.8	NR	NR	13.0	3.8	31.0	[20]
Spain	34.48	14.54	2.16	NR	18.49	5.00	25.33	[21]

NR: not reported.

It should be considered that a part of corn stover must be left on the field to maintain land fertility and avoid soil erosion. This consideration is complex and depends on different parameters such as crop rotations, tillage type, soil characteristics, climate, location, and slope [26]. Conventional harvesting and cultivation methods lead to a collection efficiency of less than 40% [27].

Corn stover harvesting could be performed wet or after drying on the field. The dry harvest includes shredding, raking, leaving to dry, windrowing, and baling the stover. These steps are multi-pass and cannot be performed with grain harvest simultaneously. Therefore, the dry harvest of corn stover is costly. Whereas in wet harvest, the required steps can be performed on the day of corn harvesting, and the corn harvester can do shredding and windrowing. Some researchers have recently focused on developing one-pass machines to provide the simultaneous harvesting of grain and stover as well as leaving the required residue on the land as a fertilizer [25,28].

Harvesting of corn stover has both good and bad results. On the one hand, this activity leads to a decrease of some diseases and pests, ease of planting with the aid of traditional equipment, and an increase in germination temperatures. On the other hand, harvesting can lead to loss of control over some other diseases, decreasing the amount of carbon and nitrogen in the soil, and increasing soil drought probability and soil erosion [29]. Therefore, finding the right amount of corn stover to be removed from the soil and the optimal amount to be left on the field is of critical importance.

In a study conducted by Karimi Alavijeh and Karimi [30], collectible wet and dry corn residue ($Q_{R,w}$ and Q_R (million tonnes), respectively) were calculated after calculating residue to product ratio (RPR) from corn yield (Y_{Corn} (t.ha^{-1})). With this data, the potential bioethanol can be calculated as follows [30]:

$$RPR = -0.138 \times Ln(100 \times Y_{corn}) + 1.8681 \tag{1}$$

$$Q_{R,w} = f_{CE}(P_{corn} \times RPR - S_{corn} \times f_{GC}) \tag{2}$$

$$Q_R = (1 - f_m) \times Q_{R,w} \tag{3}$$

$$Q_{bioethanol} = Y_{bioethanol} \times Q_R \tag{4}$$

where f_{CE} is residue collection efficiency and is assumed to be 0.35 (as conventional collection methods suggest) [31]. P_{Corn} and S_{Corn} are corn production (million tonnes), and the area that produced corn was harvested on (million ha). F_{GC} is the ground cover factor (t.ha^{-1}), and an amount of 2.7 t ha^{-1} was taken for this factor in this study [32]. F_m is moisture content by weight, and according to Baral and Shah, it is assumed to be 0.2 [33]. Bioethanol yield from corn stover ($Y_{bioethanol}$ (L. kg^{-1})) is 0.29 [32].

Based on the annual corn production of different parts of the world, the amount of corn stover and potential bioethanol can be calculated. Table 2 shows the amount of potential bioethanol in different parts of the world based on the amount of corn produced in each part during 2019 [34,35]. Approximately 43 million cubic meters of bioethanol can

annually be produced merely from corn stover from the top 10 producers in the world.

The amount of pollutant gases emitted from burning corn stover can be estimated by the formula below [36]:

$$R_b = (P \times RPR - F_{CE} \times S) \times (1 - F_{CE}) \times F_r \times (1 - F_m) \times F_{BE} \times F_b \tag{5}$$

$$E_i = R_b \times EF_i \tag{6}$$

In the formula above, R_b is the annual amount of corn stover burnt in the field (t), and E_i is the emission from the burning procedure (t). P is the amount of corn (t), and S is the area in which corn has grown (ha). F_{CE} is collection efficiency, F_{BE} is the burning efficiency and is assumed to be 0.95, F_b is the fraction of corn stover burnt and is assumed to be 0.23, and F_r is the fraction of corn stover left at the time of burning, and a value of 0.5 is taken for this value [36]. Li et al. [37] reported the emission factors for different pollutants (Table 3). To calculate region-specific emissions, further comprehensive work is required to estimate the corresponding region-specific parameters, such as the local corn stover collection efficiency and burning efficiency; in this review, fair estimates of carbon emissions on global perspective (as presented in Tables 4–5) were calculated using the same base assumptions and parameter values reported in the published literature. Table 4 summarizes the reductions in the emission of pollutants in the regions presented in Table 2 when corn stover is collected with the conventional efficiency (35%) instead of burning the total corn stover generated.

The use of first-generation ethanol as an additive to gasoline has been commercially developed in many countries. Cellulosic ethanol can replace first-generation ethanol, which can result in substantial reductions in GHG emissions and consequent social carbon costs. Social carbon costs (SCC) are defined as the costs imposed on society by each tonne of CO_2 emissions. The following formula can be used to estimate the total GHG emissions and SCC reductions based on the difference between the energy contents of ethanol and gasoline as well as applying the total GHG emission factors, known as well-to-wheel emissions factors [30]:

Table 3
Emission factors for some pollutants.

Pollutant	Emission factor (t/kt residue)
CO_2	1470
CO	60
CH_4	3.36
NMVOCs	7.48
N_2O	0.07
NH_3	0.37
SO_2	0.85
NO_x	3.3
$PM_{2.5}$	7.58
OC	2.69
BC	0.491

NMVOCs: non-methane volatile organic compounds; OC: organic carbon; BC: black carbon.

Table 2
Potential bioethanol from top 10 corn producers in the world.

Region	Corn production (million tonnes)	Area (million hectares)	RPR	$Q_{R,w}$ (million tonnes)	Q_R (million tonnes)	Potential bioethanol (million tonnes)
U.S.A	347	33.1	0.91	79.24	63.39	18.38
China	254	41	0.98	48.38	38.70	11.22
Brazil	101	18.1	1	18.24	14.59	4.23
European Union	64.56	8.5	0.95	13.43	10.74	3.11
Argentina	50.6	6.1	0.94	10.88	8.70	2.52
Ukraine	35.5	4.9	0.96	7.30	5.84	1.69
India	29	9.5	1.08	1.98	1.58	0.46
Mexico	25	6.8	1.06	2.85	2.28	0.66
South Africa	14	2.9	1.02	2.26	1.81	0.52
Russia	14	2.45	0.99	2.54	2.03	0.59
worldwide	1102	191.5	0.99	200.88	160.70	46.6

Table 4
Reductions in pollutant emissions in the top corn-producing parts of the world as a result of corn stover collection. All the values are reported in thousand tonnes of each pollutant.

Region	CO_2	CO	CH_4	$NMVOC_s$	N_2O	NH_3	SO_2	NO_x	$PM_{2.5}$	OC	BC
U.S.A.	15166.80	619.05	34.67	77.18	0.72	3.82	8.77	34.05	78.21	27.76	5.06
China	12391.64	505.78	28.32	63.05	0.72	3.12	7.16	27.82	63.90	22.68	4.14
Brazil	5070.74	206.97	11.59	25.80	0.24	1.28	2.93	11.38	26.15	9.28	1.69
European Union	3006.38	122.71	6.87	15.30	0.14	0.76	1.74	6.75	15.50	5.50	1.0
Argentina	2317.12	94.58	5.30	11.79	0.11	0.58	1.34	5.20	11.95	4.24	0.77
Ukraine	1321.11	53.92	3.02	6.72	0.06	0.33	0.76	2.96	6.81	2.42	0.44
India	1686.05	68.82	3.85	8.58	0.08	0.42	0.97	3.78	8.69	3.08	0.56
Mexico	1390.39	56.75	3.18	7.07	0.07	0.35	0.80	3.12	7.17	2.54	0.46
South Africa	726.90	29.67	1.66	3.70	0.03	0.18	0.42	1.63	3.75	1.33	0.24
Russia	694.86	28.36	1.59	3.54	0.03	0.17	0.40	1.56	3.58	1.27	0.23
World	54656	2230.85	124.93	278.11	2.60	13.76	31.60	122.70	281.83	100.02	18.26

Table 5
Reduction in GHG emissions and total social carbon costs if corn-stover-based ethanol-blended fuels replace gasoline.

Region	Δ_{GHG} (million tonnes of CO_2 eq.)	Δ_{SCC} (million dollars)
U.S.A.	41.99	1.97
China	25.63	1.20
Brazil	9.66	0.45
European Union	7.11	0.33
Argentina	5.76	0.27
Ukraine	3.87	0.18
India	1.05	0.05
Mexico	1.51	0.07
South Africa	1.96	0.06
Russia	1.34	0.06
World	106.44	5.00

$$Q_{blend} = \frac{Q_{ethanol}}{x} \tag{7}$$

$$Q_{savings} = f_e \times Q_{ethanol} \tag{8}$$

$$Q_{eq} = f_e \times Q_{ethanol} + (1-x) \times Q_{blend} \tag{9}$$

$$f_{wtw,blend} = x \times f_{WTW,ethanol} + (1-x) f_{WTW,gasoline} \tag{10}$$

$$\Delta_{GHG} = f_{WTW,gasoline} \times Q_{eq} - f_{WTW,blend} \times Q_{blend} \tag{11}$$

In the formulas above, the amounts of Q_{blend} (total amount of ethanol-gasoline blended fuel), $Q_{savings}$ (total amount of gasoline savings), $Q_{ethanol}$ (total quantity of corn-stover-based ethanol), and Q_{eq} (total amount of gasoline-equivalent to the blended fuel) are all in the unit of cubic meters. X denotes the volumetric fraction of ethanol in the blended fuel (5%: E5, 10%: E10, 85%: E85). F_{WTW} is the well-to-wheel factor (t CO_2 eq. m^{-3} fuel). This factor is 0.6 and 3 t CO_2 eq.m^3 fuel for cellulosic ethanol and gasoline, respectively [31]. Finally, f_e is the ratio of the energy density of ethanol to gasoline and is assumed 0.68 L gasoline. l^{-1} fuel [38] for this study. After obtaining the reduction in greenhouse gases emissions, carbon social costs and reduction of total carbon costs ($) can be estimated as follows [30]:

$$f_{SCC} = 1.0286 \times year - 2031.8 \tag{12}$$

$$\Delta_{SCC} = \frac{\Delta_{GHG}}{1000} \times f_{SCC} \tag{13}$$

Table 5 summarizes the total reduction in GHG emissions and social carbon costs if the available corn stover in different countries is used to produce blended fuels.

2.1.2. Pretreatment

Corn stover, as a lignocellulosic raw material, needs a pretreatment step that opens up its crystalline structure and sets the cellulose and hemicellulose free from their complex with lignin, making them accessible for further processing (hydrolysis and fermentation). Cellulose is a polymer of D-glucose molecules bonded to each other through β-(1,4) glycosidic bonds. Fig. 1 better illustrates this structure. Hemicellulose comprises various polymers of pentoses and hexoses, D-xylose pentose being the leading sugar in terms of the amount [39].

This step is the most challenging step in corn stover conversion to bioethanol and has a lot of space for improvement [40]. The pretreatment unit takes up to 16–19% of a biorefinery's capital cost [41], which needs cardinal attention. Furthermore, the pretretrement operation significantly affects the access of enzyme to cellulose and hemicellulose in a subsequent enzymatic hydrolysis step. Since the enzyme cost is a substantial contributor to the total hydrolysis cost (up to ~70%) [42], efficient pretreatment plays an imperative role in the economic feasibility of second-generation biorefineries. Different methods can be used for corn stover pretreatment, but the four main categories are physical, chemical, biological, and a combination of the first three. These methods that are categorized in Table 6, together with their generic advantages and disadvantages, are further discussed in this section. Many factors affect the choice of pretreatment method. Product yield, waste production, chemical consumption for the pretreatment and recycling ability of the used chemicals, cost-effectiveness, and the corn stover composition are the most crucial factors [43,44].

Physical pretreatment is used to decrease the particles' sizes or increase the surface area of corn stover without size reduction. Physical pretreatment is usually not sufficient but rather a step before, simultaneous with, or after another method. Milling, pyrolysis, and irradiation are noteworthy physical pretreatment methods. Particle size reduction does not change the efficiency of some chemical pretreatments like explosions. Consequently, physical pretreatment can be omitted from these processes, lowering the costs to a considerable degree. As mentioned, physical pretreatment can be used after the chemical one. In this case, it is called "post-chemical pretreatment size reduction", and has some advantages over the conventional processes, such as fewer energy requirements. However, not all pretreatments have the ability to benefit from this kind of size reduction [44].

A modification in the crystalline structure of corn stover with the aid of chemicals can occur before or after physical pretreatment and is called chemical pretreatment. Chemical pretreatments have been investigated and developed a lot [19,44–49]. Here, we will take a brief look at the most important chemical pretreatments.

Alkaline pretreatment, probably the oldest, uses alkaline solutions such as NaOH, $Ca(OH)_2$, and Na_2CO_3, and it affects lignin-carbohydrate ester bonds and hemicellulose acetyl groups in a series of reactions. The efficiency of this method depends on the solution concentration, exposure time, and temperature [41,44,50,51]. Mirmohamadsadeghi et al. [52] investigated the effect of sodium carbonate pretreatment on corn stover and reported a high glucose yield of 95% after partial delignification by this alkaline pretreatment. Zheng et al. [53] developed a wet state NaOH pretreatment and compared it with solid-state, and claimed that This method decreases pretreatment time by 86%, and 66.7% less
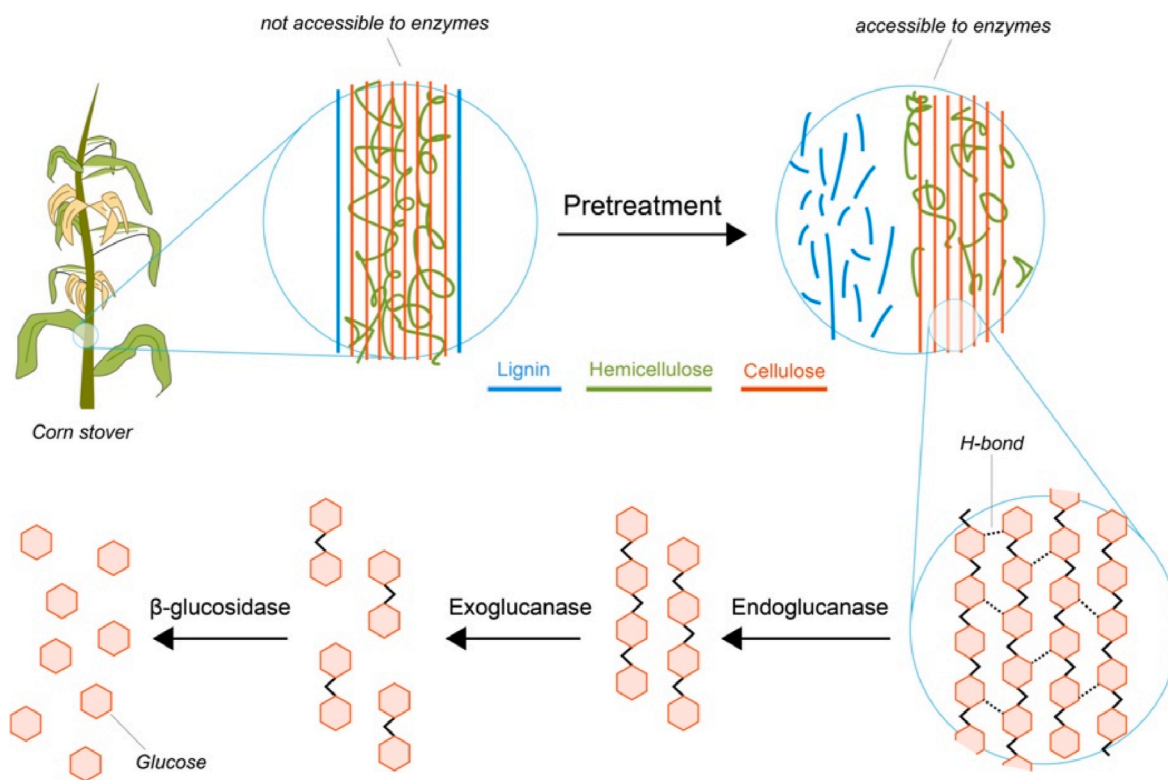
Fig. 1. Schematic of pretreatment effects.

sodium hydroxide dose than the commercial solid-state pretreatment.

Acid pretreatment has received abundant attention over the years. Steam explosion, liquid hot water, and dilute acid pretreatment are the main acid pretreatments, and they have proven to be effective on corn stover [19,41,45,46,54]. Acid pretreatment targets the hemicellulose glycosidic linkages [44]. In dilute acid pretreatment, hemicellulose is degraded to xylose and then to furfural [55]. Furfural acts as an inhibitor in the next stages [40]. After the treatment, the solid phase mostly consists of lignin and cellulose, and the liquid phase is mostly hemicellulose [44]. Yongming Zhu et al. [54] showed that a preheating step to remove moisture before dilute acid pretreatment confines autohydrolysis and results in considerably higher sugar yields. Um et al. [56] compared phosphoric and sulfuric acid for corn stover pretreatment and concluded that sulfuric acid was a better choice.

Steam explosion comprises the exposure of biomass to high temperatures and pressures and an instant decrease of pressure afterward. During the steam explosion, acetic and uronic acids are released from lignocellulosic materials that autocatalyze the saccharification process of hemicellulose. Hence, this method is considered both physical (pressure-driven explosion) and chemical (autohydrolysis). The released acids during the steam explosion are the reason for classifying this method as an acid pretreatment [57]. A chemical catalyst may be added to the steam explosion process [41]. Without using a catalyst, pH will come down to 3–4 during the process. Sulfuric acid and sulfur dioxide are among the catalysts that have been used in the steam explosion [58]. The steam explosion has been investigated on corn stover [59] and led to a decrease of 8.47%, 50.45%, and 36.65% in cellulose, hemicellulose, and lignin contents [59].

Ammonia fiber expansion (AFEX) is a catalyzed steam explosion pretreatment using alkaline ammonia at pH < 12 that leads to high sugar yields. In this method, dehydrated liquid ammonia is added to biomass at high pressures and mild temperatures (60–140 °C) for a short time (5–45 min). Afterward, the explosion occurs like the one in the steam explosion pretreatment [60]. Teymouri et al. [60] optimized AFEX pretreatment and hydrolyzed the pretreated corn stover to reach nearly 100% and 80% of the theoretical glucose and xylose yields, respectively.

Jun Li et al. [61] performed Magnesium oxide (MgO) pretreatment on corn stover and compared it with liquid hot water (LHW) pretreatment. The metal oxide MgO acts as a neutralizing agent for acetic acid, released from hemicellulose in the pretreatment slurry, and it prevents producing furfural and HMF. MgO pretreatment resulted in double hemicellulose recovery, better lignin removal, and an increase of sugar yield by 6%, compared to LHW pretreatment. This pretreatment lasted 40 min at 190 °C [61].

Organosolv pretreatment uses organic solvents in the absence or presence of a catalyst (salt, base, or acid). Organosolv pretreatment can fractionate lignocellulose to cellulose, hemicellulose, and lignin; thus, it is able to yield multiple products that are interesting for biorefinery development [62–64]. The other advantage of this method is the minor degradation of cellulose and hemicellulose and the simple possibility of organic solvent recovery by distillation [63]. In organosolv pretreatment, the biomass is treated with an organic solvent (usually alcohols, especially the normal primary ones such as ethanol and methanol) to partially hydrolyze lignin and carbohydrate-lignin bonds. This leads to a solid residue that is mainly composed of cellulose and small amounts of hemicellulose. After delignification, cellulosic fibers are separated with filtration and are washed with solvent and water. The liquid phase of the filtration is sent to a distillation unit to separate the organic solvent. Water is added to the remaining black liquor to precipitate lignin. Another filtration process then separates lignin from hemicellulose sugars [63]. Qing et al. [65] performed a two-step pretreatment on corn stover. They soaked corn stover in an alkaline solution and then used organosolv pretreatment (using 20% methanol and 0.2% HCl as a catalyst) for 20 min. This method resulted in a 98.6% sugar yield [65].

A newly-developed pretreatment method is performed using ionic liquids [66]. Ionic liquids can metabolize both softwoods and hardwoods and have proven to be very effective for corn stover pretreatment [66,67]. In this method, an ionic liquid is added to biomass and is heated until the biomass dissolves in the liquid. Then a precipitating agent (water or alcohol) is added to separate a glucan-rich phase. The

Table 6
Main characteristics of pretreatment methods.

Pretreatment	Advantages	Disadvantages	Reference
Alkaline	1) Low interaction with hemicellulose. 2) Efficient delignification. 3) Mild conditions	1) not as much effective on recalcitrant species. 2) Conversion of alkali to salts not coverable. 3) Concerns about the alkali if released into the environment.	[80,81]
Dilute acid	1) High yields of saccharification 2) Solubilizing hemicellulose 3) Flexible method.	1) Production of inhibitory substances. 2) Corrosiveness of acid. 3) High cost of acid recovery.	[82]
Steam explosion	1) Low cost. 2) Easy hemicellulose delignification and saccharification. 3) Cellulose crystallinity disruption.	1) Partial hemicellulose solubilization. 2) Production of toxic compounds. 3) Generation of inhibitory substances to microbial growth. 4) Incomplete breakage of lignin-carbohydrate bonds.	[83]
AFEX	1) Short pretreatment time. 2) No inhibitor generation. 3) Up to 99% sugar recovery. 4) No further steps like washing or particle size reduction are needed.	1) Toxicity 2) Intense operating condition. 3) Not much effective on raw materials with high lignin content.	[84]
Organosolv	1) High fermentation yield. 2) High fractionation of hemicellulose. 3) Cellulose recovery with high purity. 4) Capability to recover pure lignin as a solid.	1) High costs. 2) Very energy-intensive to recover organic solvents. 3) Pretreated solids should be washed with an organic solvent prior to washing with water.	[63]
Ionic liquids	1) Mild operating conditions. 2) Almost 100% recovery. 3) Up to 100% hemicellulose solubilization. 4) Green in nature and not hazardous.	1) Generation of inhibitors. 2) High cost. 3) Difficulty in recovery. 4) Toxic to some microorganisms. 5) Difficulty in lignin and hemicellulose extraction.	[70,85]
Biological	1) Mild operating conditions. 2) Low energy consumption. 3) No recycling activities are needed. 4) Minimum inhibitory substances generation.	1) Long pretreatment time. 2) Low downstream yields. 3) Carbohydrate losses.	[86]

remaining liquid is further processed to recover ionic liquids [68]. Uppugundla et al. [67] compared three pretreatment methods and reached 90% lignin removal from corn stover using this method. On the other hand, they concluded that, unlike AFEX, ionic liquid and dilute acid pretreatments required nutrients supplementation because of the loss of nutrients that happened during these methods [67]. Geng and Henderson [69] combined mild alkali pretreatment with ionic liquids and then hydrolyzed the pretreated corn stover. This method led to a 96% glucose yield [69].

Deep eutectic solvents (DESs) are biocompatible and promising ionic liquids that are composed of hydrogen donors and quaternary ammonium salts. The reason why deep eutectics are a separate category from ionic liquids is that they can be composed of non-ionic liquids as well [70]. Seven different DESs were investigated on corn stover by Guo-Chao Xu et al. [71], and after optimization, 99% glucose yield was reached. To further improve this method of pretreatment, microwave-assisted DES is being developed that decreases the pretreatment time considerably [72].

Biological pretreatment is a safe and environmentally friendly process that is performed by lignocellulose-degrading microorganisms to improve the digestibility of corn stover. Fungal, microbial consortium, and enzymatic pretreatments are different biological processes that can be used upstream of biofuel production from corn stover [73]. Soft- and brown-rot fungi mostly degrade cellulose, while white-rot fungi utilize lignin [74]. Extracellular enzymes are produced by these organisms to increase the digestibility of cellulose and hemicellulose. Lignin peroxidases and laccases are examples of enzymes degrading lignin. Biological pretreatment is not energy-intensive [41]; however, it is time-consuming and needs large facilities and equipment [73]. Different biological pretreatments have been performed on corn stover [18,75, 76]. Lili Song et al. [77] provided a conventional biological pretreatment using *Irpex lacteus* in the presence of manganese ions. Then, they compared the conventional method with their method, i.e., the addition of manganese to the conventional one, and determined the hydrolysis yield after these two pretreatments. Their proposed method showed a glucose yield of 61.39% higher than the conventional biological pretreatment [77].

A combination of different pretreatment units can result in higher yields and needs precise economic analysis. For instance, a combination of steam explosion and alkali treatment can function more effectively than single pretreatments since each method targets specific linkages [44].

Comparisons between steam explosion, AFEX, dilute sulfuric acid and biological pretreatments reveal that biological pretreatment requires twice as more feedstock as sulfuric acid, and it needs more than 10 times capital investment compared with the other methods under study. Operating costs are also twice for biological pretreatment, implying it needs more development before being industrialized. In terms of external energy needed, ammonia fiber explosion requires 4 time as energy as dilute sulfuric acid, while biological pretreatment needs one fifth of this amount [42].

In terms of environmental issues, utilization of greener solvents like DESs, ionic liquids and supercritical fluids seems more promising, although these methods need more research before industrialization. Deep eutectic solvents are the most promising among these strategies as they are more environmentally friendly and cost effective [78].

In an interesting study, Smullen et al. [79] did an LCA study on four pretreatment methods, namely, NaOH, Ammonia, sulfuric acid, and methanol in different categories. Regarding global warming potential, methanol showed to be by far the best strategy, while it was the worst in terms of eutrophication. Overall, ammonia and methanol were the best options for air, soil and water, while sulphoric acid and NaOH dominated global warming, eutrophication and photochemical oxidation demand [79].

2.1.3. Saccharification

Saccharification (hydrolysis) is the process in which cellulose and hemicellulose, now more accessible after pretreatment, are converted into hexoses and pentoses. Cellulose is converted into glucose, but hemicellulose into different pentoses and hexoses in case of complete hydrolysis. The conventional hydrolysis methods are chemical and enzymatic hydrolysis. Some other approaches may be performed for lignocelluloses hydrolysis, including microwave and electron-beam irradiation and gamma-ray hydrolysis [87].

Acids, especially sulfuric acid, are the leaders in chemical hydrolysis. Both dilute and concentrated acids are available in functioning saccharification processes. Concentrated acid saccharification results in a higher sugar yield and can be operated at lower temperatures. On the other hand, dilute acid needs shorter residence times to carry out the saccharification [87]. Although chemical saccharification is being used around the world, all the reviewed papers in this paper used enzymatic saccharification for corn stover [18,19,45,49,75,76].

Enzymatic saccharification is carried out mainly by cellulases. Cellulolytic enzymes speed up the enzymatic saccharification. Enzymatic saccharification has the merits of higher yields and fewer inhibitory byproducts compared to chemical hydrolysis. On the other hand, dilute-acid saccharification consumes less time and costs, two cardinal factors in industrial processes. Besides, the released sugars play inhibitory roles in enzymatic hydrolysis [88]. Enzyme loading is a key factor that should be carefully optimized in enzymatic hydrolysis due to the high price of the enzyme. In addition, if this parameter exceeds a certain limit, overcrowding of the enzyme molecules plays an inhibitory role in the fermentation [89]. Table 7 summarizes some different studies on corn stover pretreatment and saccharification. Zhu et al. [54] investigated the effect of enzyme loading on sugar digestibility of dilute-acid pretreated corn stover and reported sugar yields of 92%, 98%, and 80% for 5, 15, and 40 FPU/g of glucan, respectively [54].

Although laboratory-scale studies choose enzymatic saccharification over chemical ones, the high prices of enzymes hinder its industrial use. Ma and Ruan [90] conducted an entirely new experiment in which they co-cultured *Coprinus comatus* with *Trichoderma reesei* and performed simultaneous biological pretreatment and hydrolysis in a single bioreactor. This method resulted in 66.5% lignin degradation and 82% sugar yield. They claimed that this method could lead to less expensive enzymes for large-scale productions [90].

2.1.4. Fermentation

Fermentation includes the bioconversion of the produced monomers (mainly glucose and xylose) to bioethanol, biobutanol, etc. The focus of this paper is bioethanol. Fermentation is carried out by a vast diversity of bacteria or yeasts, fungi, and algae [91].

Saccharomyces cerevisiae is the most used yeast for fermentation, which cannot metabolize pentoses. Since hemicellulose is an important part of lignocellulosic materials and it contains pentoses, it is important to work around this major issue. Nowadays, recombinant yeasts and fungi with the ability to metabolize both hexoses and pentoses are being introduced to the world [91], like the attempts to modify *S.cerevisiae*. *Pichia stipitis* is an example of yeast able to ferment both hexoses and pentoses. Some bacteria like *Escherichia coli, Lactobacillus, Clostridia, Bacillus, Erwinia*, and *Klebsiella* have also been proposed because of having the same advantage, but they do not give high ethanol yields [92].

Fermentation can be categorized into two types: submerged and solid-state fermentations. Submerged fermentation refers to the type that microorganisms grow in a liquid medium. This strategy has reasons to be favorable, like the ease of changing the conditions of the medium, for example, pH or temperature. Other than that, it is easy to maintain uniform conditions throughout the medium by mixing. The technologies needed for this strategy are also well-developed [92]. Ethanol is one of the most important products of this fermentation strategy.

Different combinations of saccharification and fermentation with each other make different process types; separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), non-isothermal simultaneous saccharification and fermentation (NSSF), and simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing are the five categories in which the plants can work. In SHF, polymers are hydrolyzed to monomers and then further processed to bioethanol in a separate unit. Since a high concentration of sugars plays an inhibitory role in enzymatic saccharification [93], one solution to this problem is SSF, in which performing the hydrolysis and fermentation in a single unit provides utilizing the sugars immediately after production and improving the ethanol yield. Optimizing the temperature in a way that both these stages work in near-to-maximum yields is the main challenge in SSF. This problem is solved in the NSSF process, in which saccharification and fermentation occur at the same time but in two different reactors at two different temperatures. SSCF refers to a process that ferments both pentoses and hexoses, so hemicellulose and cellulose are fed to the hydrolysis and

Table 7
Different studies on corn stover pretreatment and enzymatic saccharification.

Pretreatment			Duration	Lignin degradation	Sugar yield		Study
Chemical	Lime		28 d	87.5%	Glucose	Xylose	[45]
					93.2%	79.5%	
	Steam		5 min	48%	96%	74%	[19]
	Liquid Hot Water		NR	NR	90%	NR	[46]
	Organosolv		30 min	81.7%	83.2%	NR	[47]
	Dilute Acid		5 min	NR	92.5%	NR	[48]
	Alkaline	NaOH	24 h	46.2%	NR	NR	[51]
		Na₂CO₃	3 h	58.6%	95.1%	NR	[52]
	Ionic liquid		3 h	90%	NR	NR	[67]
	Deep eutectic solvents (DES)		2 h	23.8%	99%	NR	[71]
	Microwave DES		45 s	80%	78.5%	55%	[72]
	Aqueous Ammonia (60 FPU/g of glucan)		20 min	85%	99%[a]		[49]
	Aqueous Ammonia (10 FPU/g of glucan)				92.5%[a]		
Biological	*Cyathus stercoreus NRRL-6573*		30 d	46.2%	64%	35%	[75]
	Pycnoporus sanguineus FP-10356-Sp			51%	57%	45%	
	Phlebia brevispora NRRL-13108			38%	51%	48%	
	Trametes hirsute yj9		7 d	14.95%	22.05%[a]		[76]
			14 d	41.74%	46.78%[a]		
			21 d	54.22%	67.29%[a]		
			28 d	59.5%	68.64%[a]		
			35 d	66.83%	70.75%[a]		
			42 d	71.99%	73.99%[a]		
	Ceriporiopsis subvermispora				Glucose	Xylose	[18]
			18 d	31.59%	57.67%	30.40%	
			28 d	NR	62.21%	36.88%	
			35 d	NR	66.61%	38.21%	

NR: not reported.

[a] Values reported as overall sugar yield, not distinguished between glucose and xylose.

fermentation reactor without separation [88]. Consolidated bio-processing performs all enzyme production, enzymatic hydrolysis, and co-fermentation in a single-phase and has attracted many researchers recently [94].

Different categories of hydrolysis and fermentation have been investigated for corn stover [95–97]. Öhgren et al. [95] compared SSF and SHF for steam-pretreated corn stover and concluded that SSF has a higher ethanol yield (72.4%) than SHF (59.1%) [95]. In another study, Öhgren et al. used recombinant *Saccharomyces cerevisiae TMB 3400* with the ability to ferment xylose and reached 59% of the theoretical ethanol yield in an SSF process [96]. Liu and Chen [97] took advantage of another recombinant xylose-fermenting strain, *Saccharomyces cerevisiae IPE003,* in an SSCF process to reach ethanol yields of higher than 90% in different glucose/xylose ratios and fermentation times. They also concluded that increasing solid loading results in a decrease in ethanol yield, down to 75% yield in 20% solid loading [97]. Using fungi such as *Coniochaeta ligniaria* NRRL30616 can degrade the fermentation inhibitors and improve ethanol productivity [98].

The parameters introduced until now, namely corn stover composition, pretreatment, hydrolysis, and fermentation, affect the produced bioethanol to a considerable degree. The potential bioethanol that can be produced is calculated based on the yield of each of these stages. To this end, the overall ethanol yield is decomposed into several components as shown by Eq. (14) [31]:

$$Y_{eth} = x_C \times r_C \times h_h (1 - l_h) y_h \tag{14}$$

It is noteworthy that the above formula is only valid for the microorganisms that can only ferment hexoses. If the microorganism is capable of degrading pentoses as well, another term would be added to the formula to take that into consideration as well. x_C is the amount of cellulose in corn stover, r_C is the efficiency of pretreatment, h_h is the yield of hydrolysis of hexoses, y_h is the yield of fermentation that can be as high as 0.5, and a minimum quantity of 0.3 for this is assumed here. L_h is the amount of sugar lost in the process and is assumed as 0.1 [31]. Based on the papers studied here, x_C can vary from 0.32 [18] to 0.38 [20], r_C from 0.24 [71] to 0.9 [67], and h_h ranges from 0.5764 [18] to 0.98 [99]. When assessing the effect of each process parameter, all the other parameters are taken as averages or conventional quantities. For example, cellulose content in the corn stover is taken as 0.36, y_h is taken as 0.46, which is the fermentation yield for S.cerevisiae [100], and pretreatment and hydrolysis yields are taken as 0.91 and 0.88 from a study by Kim and Dale [45].

Fig. 2 shows the potential bioethanol in the world that can be produced from corn stover under the worst- and best-case scenarios for each of these parameters to show how each of them affects bioethanol production.
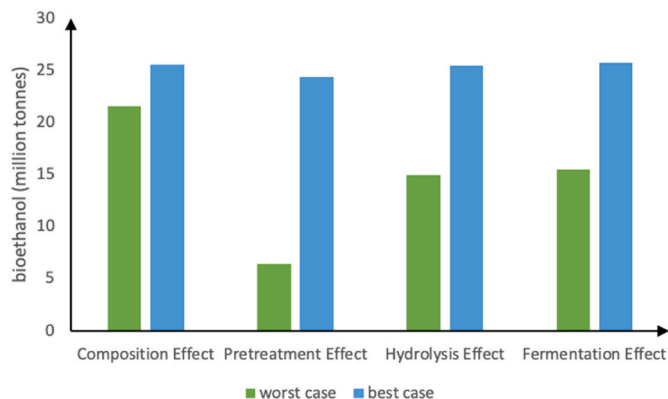

Fig. 2. Effect of process parameters on the potential global amount of bioethanol from corn stover.

2.1.5. Ethanol uses

Ethanol is being widely used all over the world in medicines, production of perfumes, flavors, and varnishes [101]. More than 98 billion liters of ethanol were produced in 2020, proceeding the 110 billion liters in 2019. Fuel production is the main sector where ethanol is being used. In 2019, The U.S. alone produced approximately 60 million liters of fuel ethanol [102].

As a biofuel, ethanol can be blended with different fuels with different percentages. Regarding gasoline, numerous ethanol blends have been introduced for engine uses. For every 10% of ethanol that is added to the blend, the octane number increases by 5% [103]. F.Yüksel and B.Yüksel [104] compared the power output and emissions of gasoline with ethanol-gasoline fuels. Their observation was that CO and HC emissions decreased by 80% and 50%, respectively, but the power output decreased slightly as well [104]. The most famous blends are E10, i.e., 10% ethanol in the blend, E15, and E85. Based on the U.S. Environmental Protection Agency (EPA) [105], E10 can be used instead of gasoline in any normal engine. E15 is practical for the 2001 and newer vehicles. Flexible fuel vehicles (FFVs) are able to use up to E85 blends [105]. Finally, the E100 blend needs special engines, and producing E100 blends is only possible in plants that are approved as beverage producers and pay the beverage alcohol tax. Besides, gasoline contains many components, some of which are vapor even at low temperatures, thus enabling the engine to ignite the fuel-air mixture and start at these temperatures [106]. The distance driven by a car with bioethanol fuel is less than gasoline. In a study, Dan Edmunds et al. [107] drove 667 miles (from San Diego to Las Vegas and the other way around), once by gasoline, and another time by E85, using the same car. The gasoline used for this distance was approximately 138 L. However, the E85 had a lower fuel economy; 189 L of this fuel were needed to travel the same distance [107].

Bioethanol can be mixed with diesel as well. Bilgin et al. [108] used three different blends on conventional diesel engines and concluded that a fuel consisting of 3.5% ethanol with a compression ratio of 21 increases the power of the engine compared with diesel fuels. Ajav et al. [109] used 5, 10, 15, and 20% ethanol-diesel blends and observed negligible differences in the engine power compared with diesel fuel. In another study, Sayin [110] compared E5 and E10 with diesel and observed a decrease of CO emission by 7.1% and 24.2% in comparison with diesel, a decrease of 34.3% and 40% in total hydrocarbon emission, and an increase of 11.3% and 13.1% in NO_x emission. Sayin also tested BSFC (the ratio of mass fuel consumption to the brake power). Diesel showed the lowest amount (298 g/kWh), with E5 and E10 having BSFC values of 304 and 316, meaning blended fuels have smaller lower heating values (LHVs) [110].

As mentioned, bioethanol increases the octane number of fuels. Methyl *tert*-butyl ether (MTBE) was previously used for this goal and is still being used in some countries. However, due to its contaminating effects on groundwater, this substance has been eliminated and replaced by bioethanol in the USA [111].

Lastly, it is noteworthy that methanol is another option to be added to fuels, but ethanol is usually preferred because of toxicity issues and ethanol being more renewable [103].

2.1.6. Biorefinery development based on corn stover

To increase the efficiency of ethanol production from corn stover, the biorefinery concept can be applied to it. A biorefinery is a facility that can convert corn stover into power, chemicals, and fuels [112]. Biorefinery development is a way to make ethanol production more comprehensively and integrate it with the production of other high-value chemicals and electricity. Fig. 3 shows bioethanol production process coupled with heat and power production.

Biorefineries are categorized into phase I, phase II, and phase III biorefineries. Phase I biorefineries take advantage of a single feedstock (corn stover here) and convert it into a single product. In order to have a phase II biorefinery, the corn stover should be converted to different
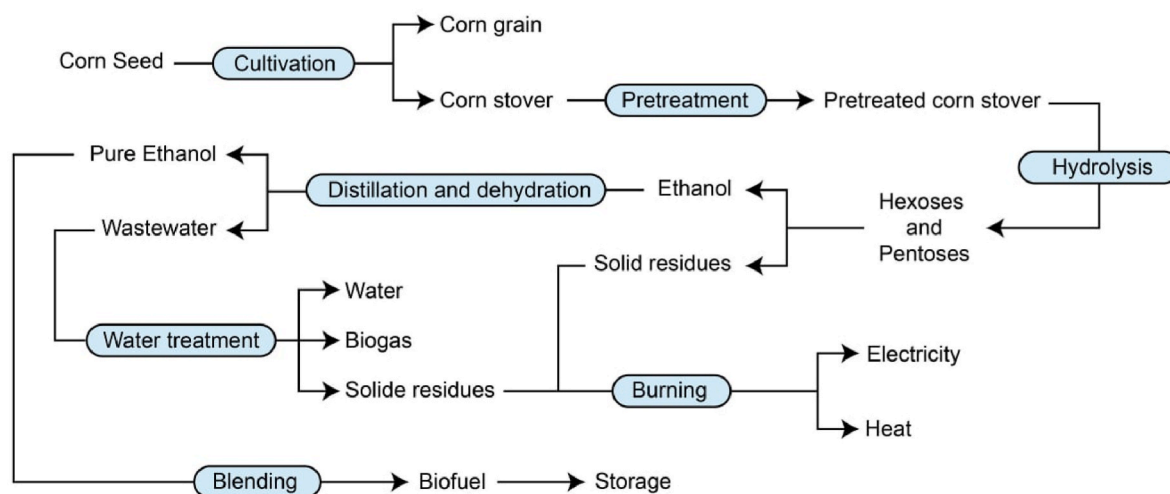
Fig. 3. Ethanol production process from corn stover.

products. Finally, in phase III, corn stover is coupled with other feed-stocks, and several products are produced simultaneously, making it a very complicated combination of processes but very effective at the same moment [113].

In order to have an effective biorefinery, fractionation of the different substances after pretreatment becomes much more important since each of these substances produces a different product. Lignocel-lulose is fractioned into its building parts, lignin, cellulose, and hemi-cellulose. An effective pretreatment is the one that produces no inhibitors for further processing of the feedstock and makes the sepa-ration and recovery of the three fractions feasible [113].

The sludge from wastewater treatment, as well as lignin from the solid phase, can be burned to produce heat. This energy can be con-verted to electricity and meets the biorefinery electricity needs, and the extra heat can be sold to the energy market as a co-product [114]. This electricity production is very attractive because it can lower the envi-ronmental impacts of the process to a considerable degree [40].

High purity lignin, separated during the process, is a value-added product that can be converted to phenolic compounds (like alkox-yphenols and alkylphenols) used for many drugs and bioplastics, guaiacol (used for producing flavor agents like vanillin), and carbon fibers (used in the automotive industry) [115]. Vanillic acid and vanillin alcohol are two more value-added products from lignin that can be used as raw materials for epoxides/resins and plastics, respectively. Syngas and bio-oil can be produced from lignin as well. Carboxylic acids and benzoquinones, and catechol are more examples of numerous products from lignin [113]. The production of thermoplastics from lignin through fractionation with methanol or formaldehyde crosslinking has also been investigated [116].

Stiefel et al. [117] compared electrochemical depolymerization of lignin with the conventional methods that make use of severe conditions like high pressure and temperature and claimed the electrochemical conversion is needless of such conditions. On the other hand, this method is unselective and performed on the surface; therefore, it is dependent on the electrode structure. Electrochemical conversion of lignin in this study yielded many value-added chemicals like dibutyl phetalate, acetovanillone, 1,2-benzenedicarboxylic acid, coniferyl alcohol, etc. [117].

Hemicellulose is an important raw material for the production of many value-added chemicals, just as lignin. Lactic acid is the most important product from hemicellulose that can be further processed to yield pharmaceuticals, biopolymers, and cosmetics. Xylitol, xylooligo-saccharides, 2,3-butanediol and furfural are more crucial products that can be obtained from hemicellulose in corn stover [113,118].

Another product that a biorefinery can make is acetone-butanol-ethanol (ABE). ABE is mainly composed of butanol, so it can be used as a solvent or a fuel [119]. The main bacteria used for the fermentation of hydrolyzed corn stover to produce ABE is *Clostridium acetobutylicum* [120].

Hernandez and Siew Ng [121] compared two biorefinery systems for corn stover: ABE route and GMA (gasification and mixed alcohols) route. Their final finding was that the latter was more favorable in terms of GHG emissions (46.2 g CO_2 eq/GJ for ABE and 19.0 g CO_2 eq/GJ for GMA). However, in terms of biofuel production cost, the former pathway was more promising (49.2 and 69.9 US$/GJ, respectively), and that means ABE route is more feasible, being economically favorable in comparison to gasoline (85 g CO_2 eq/GJ), although not as environ-mentally friendly as GMA [121].

Wang et al. [122] analyzed the effect of corn stover biorefinery size on the costs. They compared three scenarios, small scale (175 dt/day), medium-scale (520 dt/day), and large scale (860 dt/day). The first result was that due to the increase in transportation, corn stover delivered cost increased from 82.09 $/dry tonne to 87.49$ and 93.75$ as the bio-refinery expanded in scale to MS and LS. Furthermore, land needed for storage got larger by 225% and 425% in MS and LS, respectively, in comparison with the small-scale biorefinery. Another outcome of this study was the huge increase in capital costs from 6.72 million dollars for a small-scale biorefinery to 21.83 for medium scale and 35.51 for large scale [122].

Bbosa et al. [120] conducted a study to assess the economic feasi-bility of a corn stover biorefinery. In their proposed method, they considered the production of acetic acid, furfural, catechol, cresols, phenol, acetaldehyde, and formic acid through liquefaction of lignin, in addition to ethanol production. This biorefinery concept lowered the minimum ethanol selling price to half its value for merely ethanol pro-duction (from 2.15 $/gal to 1.03), unveiling the huge advantage of biorefinery integration into bioethanol production from corn stover [120].

3. Techno-economic assessment

One of the most important factors that determine whether a process is feasible or not is the economics of the process. The techno-economic analysis is the tool that analyzes the viability of the processes in their development phase to determine the technical and economic perfor-mances [123].

Although second-generation ethanol production from corn stover has the advantage of producing electricity and having fewer impacts on the environment, its economics is not a factor to be sneezed at. Most of the studies consider the nth plants (plants with mature technologies) for

their assessments; nevertheless, the costs are still high for second-generation ethanol production due to the pretreatment stage and its capital and running costs [124]. Different techno-economic assessments have been performed on ethanol production from corn stover [124,125]. Feedstock cost has shown to be the most important factor that influences the minimum ethanol selling price (MESP), with enzyme cost and installed equipment costs being the next factors [124–126]. Many studies present the MESP and total capital investment as profitability parameters and use them for comparison of their results. MESP is calculated based on the calculation of the ethanol selling price, which results in a zero net present value (NPV) for the cash flow diagram. Thus, this value shows the ethanol selling price at which the plant has zero profit. MESP highly depends on the cash flow parameters, e.g., interest rate, tax rate, plant life, capital costs and operating costs and escalation factors for equipment, products, and raw materials. Therefore, careful attention to details and economic parameters is necessary for the comparison of MESP from different studies [126–128]. Below some recent techno-economic studies based on corn stover are compared, and the economic details are presented in Table 8.

Longwell Ou et al. [125] did a study on six different scenarios for ethanol production from corn: using corn grain, corn stover, and mixtures of these two feedstocks with stover-to-grain mass (SGM) ratios of 0.4:1, 0.6:1, 0.8:1, and 1:1 as the scenarios A to F, respectively. For scenarios C to F, they used co-located corn grain and corn stover facilities in order to reduce the production cost and life cycle emissions of each individual plant. They assumed the plant lifetime to be 30 years. The reported MESPs for the six scenarios were 0.55, 0.99, 0.65, 0.67, 0.68, and 0.69 dollars per liter, respectively. Their sensitivity analysis

showed that feedstock price was the main factor affecting MESP. As the SGM ratio gets bigger, the surplus electricity does so too, but it is noteworthy that at least 40% of the stover should be left on the field for sustainable harvesting to be obtained. The scenario B plant, with an ethanol production capacity of almost half of scenario A's, has a total investment cost and a total equipment purchase cost of more than three times the scenario A plant (373.16 and 123.56 MM$, respectively) [125].

Kazi et al. [124] investigated five pretreatment scenarios (low solid loading dilute-acid (base case), high solid loading dilute acid, 2-stage dilute-acid, hot water, and AFEX. Furthermore, three different downstream scenarios of pervaporation, separate 5-carbon and 6-carbon sugars fermentation, and on-site enzyme production were studied for the base case. In Table 8, the details of economic parameters used for this study are presented. In this study, product value is presented as the profitability parameter for comparison of the scenarios. This value is a synonym for MESP since the net present value of zero and 10% rate of return was used for its calculation. Dilute acid pretreatment achieved the lowest product value ($1.36/L of gasoline-equivalent or $5.13/gasoline gallon equivalent (GGE)), and hot water pretreatment showed the highest ($1.17/L). On-site enzyme production was the only technology that had a negative electricity export (−0.8 million dollars per year). Total capital investments were the lowest for hot water pretreatment and dilute-acid pretreatment and the highest for pervaporation and on-site enzyme production. In terms of total installed equipment costs, all cases were almost close to each other, except pervaporation distillation and on-site enzyme production, deviating from other cases in positive amounts. In general, this study showed that

Table 8
Assumptions used for techno-economic analysis of Corn stover.

MESP ($/L)	Total Capital Investment (MM$)	Plant Capacity (Mgal/year)	Interest rate (%)	Project life (year)	Location	Pretreatment type and scenario details	Income tax rate (%)	Other process details	Ref.
0.56[a]	187	95.9 (grain: G)	10	30	USA	Dilute sulfuric acid pretreatment for stover	39	Overliming by ammonia for second-generation ethanol Fermentation by recombinant Z.mobilis	[125]
0.99[a]	622	2233 (stover: S)				Electricity generation from wastes			
0.65[a]	546	0.4:1 (S/G)							
0.67[a]	645	0.6:1 (S/G)							
0.68[a]	731	0.8:1 (S/G)							
0.69[a]	809	1:1 (S/G)							
0.90[b]	376	2000 stover	10	20	USA	Base case: Dilute-acid (low solid 18%)	NS	All scenarios include waste incineration for electricity production. Only *Z.mobilis* was used for fermentation in all scenarios except scenario 7, in which Yeast and *Z. mobilis* were used separately.	[124]
0.95[b]	389					Dilute-acid (high solid 29.6%)			
1.17[b]	391					Two-stage dilute-acid			
0.97[b]	327					Hot water			
1.16[b]	386					AFEX			
0.94[b]	501					Pervaporation			
0.97[b]	386					Separate fermentation of C5 and C6 sugars			
0.99[b]	434					On-site Enzyme production			
1.52[a]	511					Pioneer plant (base case)			
0.693	384	2000 (dry metric tonne)	10	25	–	Dilute sulfuric acid pretreatment	37	Condition: Ammonia	[126]
0.651	316					Dilute sulfuric acid pretreatment		Condition: Lime	
0.27	624	2000 (dry metric tonne)	10	30	USA	Dilute sulfuric acid pretreatment Hydrothermal liquefaction of 80% lignin for byproduct, 20% of lignin for heat and power	0.7% of FCI	lignin-derived byproducts, e.g., cresol, acetic acid, and catechol	[120]

[a] The values reported in the table ($/L of ethanol) were calculated from the original value in $/gal of gasoline-equivalent ($/GGE), which presented in the paper by Ou et al. The product value ($/L) is calculated by dividing $/gal gasoline-equivalent value ($/GGE) by (1.51*3.785). The number 1.51 is calculated by dividing the lower heating values gasoline (32.0 MJ/L) to ethanol (21.2 MJ/L).

[b] The values reported in the table ($/L of ethanol) were calculated from the original value in $/L of gasoline-equivalent ($/LGE) which presented in the paper by Kazi et al. The product value ($/L) is calculated by dividing $/L gasoline-equivalent value ($/LGE) by 1.51. The number 1.51 is calculated by dividing the lower heating values gasoline (32.0 MJ/L) to ethanol (21.2 MJ/L). In the research by Kazi et al. product value is analogous to MESP.

dilute-acid pretreatment is the most favorable in terms of product value but is not the most effective one. This study also did a price elevation study considering pioneer technologies for bioethanol production from corn stover, and the price for the dilute-acid pretreatment went up to $2.30/L of gasoline-equivalent with the TCI rising up to more than two times the nth plant [124]. More recent pretreatments have a long path ahead to become economically beneficial, but since they lead to higher sugar and ethanol productions, they may be commercialized in the near future.

Chovau et al. [126] reviewed the most important parameters affecting MESP of ethanol, i.e., feedstock price, ethanol yield, enzyme cost, fixed capital investment, and parameters used in the cash flow analysis. This review indicates that although lignocellulosic materials are inexpensive, they contribute to 30–40% of the MESP of lignoethanol. They claimed that harvesting and collection, and grower payment are the main contributors to corn stover price. Among different pretreatment types, dilute sulfuric acid was presented as the most economically feasible. This research also compared the overliming process with ammonia conditioning, which is used to detoxify the pretreated slurry. They concluded that replacing lime with ammonia is unjustifiable in terms of MESP ($0.693 and $0.651 per liter for lime and ammonia, respectively) [126].

Although first-generation bioethanol is still the preferred process by investors, this may change as more effective pretreatments are being discovered. The price of enzymes and pretreatment facilities decrease, cheaper technologies might develop for pretreatment of corn stover pretreatment, and the governments will hopefully develop policies supporting producing-ethanol-from-corn-stover-alike plants to remove the economic obstacles. Since dent corn is the kind being used for ethanol production and it is non-edible for humans, co-located corn grain and corn stover plants are the most promising plants for the time being [125]. A corn stover biorefinery integrated with other value-added byproducts significantly enhances the future and economy of ethanol from corn stover. An example is hydrothermal liquefaction of the solid residues for the production of value-added co-products, i.e., cresols, catechol, acetic acid, phenol, formic acid, furfural, and acetaldehyde [120]. The MESP for this biorefinery was 1.03 $/gal (0.27 $/L) in spite of the high total investment cost of $624.5 MM. Based on the current trend of the oil market, the future of commercial ethanol production from corn stover highly depends on the production of value-added byproducts from the plant residual.

4. Concluding remakes and future directions

Second-generation bioethanol, although more environmentally favorable than the first generation, is not competitive enough to its counterpart due to economic reasons. Pretreatment, hydrolysis, and fermentation are the three main stages of converting corn stover to bioethanol, and there is no single method for each of these stages to be the best one. The choice can be different in any region of the world based on the available technology, environmental regulations, the price of required equipment and materials, and even the scale of the plant under study. More research is needed to increase the efficiency of these methods, especially pretreatment. A biorefinery approach is another way of decreasing the costs of bioethanol production from corn stover. Lignin and hemicellulose are valuable raw materials in many industries. Electricity production in an amount that meets the plant's demands and goes beyond is interesting too. These are also other interesting features of developing the biorefinery concept that need further research. Policies set by governing bodies also influence how fast the world moves towards second-generation biofuels.

The USA produces around 31.5% of the world's corn; thus, 23 billion liters of ethanol could potentially be produced with the corn stover that is more than 44% of its current ethanol production and about 24% of the world's production. Results for the European Union are interesting as well since it can produce 83% of its ethanol production from corn stover,

while it is mostly being produced from wheat, corn, and sugar beet [129–131]. If these two regions used their full potentials in this regard, 18 million tonnes of CO_2 emissions due to the current burning practice of corn stover would be prevented. Moreover, more than 49 million tonnes of CO_2 equivalent emissions would be further prevented from not burning fossil fuels.

Over 36 billion tonnes of CO_2 are being emitted into the atmosphere each year, and every solution to reduce these emissions out of criticality is of value [132]. The results indicated that there is a huge potential to produce bioethanol from corn stover and lower the emissions of different pollutants both by substituting the bioethanol with fossil fuels and not burning the stover in the fields.

Declaration of competing interest

The authors declare that there is no conflict of interest.

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