Bioconversion of Wood Waste to Bio-ethylene: A Review

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Bio-based ethylene produced by bioethanol dehydration is an environmentally friendly substitute for oil-based ethylene. It is a low-pollution raw material that can be used to produce high-value bio-based materials. Currently, some industrial plants use first-generation (1G) bioethanol to produce bio-ethylene. However, second-generation (2G) bioethanol is not currently used to produce bio-ethylene because the manufacturing processes are not optimized. The conversion of lignocellulosic biomass to bio-ethylene involves pretreatment, enzymatic hydrolysis of carbohydrates, the fermentation of sugars to ethanol, ethanol recovery by distillation, and ethanol dehydration to ethylene. This work presents a review of second-generation (2G) bio-ethylene production, analyzing the stages of the process, possible derivatives, uses, and applications. This review also contains technical, economic, and environmental considerations in the possible installation of a biorefinery in the northeast region of Argentina (NEA).

Keywords: Biorefinery; Lignocellulosic biomass; Bioethanol; Bio-ethylene

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INTRODUCTION

Ethylene is a chemical building block that is heavily employed in the petrochemical sector. Ethylene is traditionally obtained by cracking of the hydrocarbons from petroleum using steam (Kniel *et al*. 1980) and is recovered from refinery cracked gas (Zimmermann and Walzl 2000). In recent years, researchers have focused on sustainable alternatives to ethylene to decrease greenhouse gas (GHG) emissions and reduce the dependency on fossil fuels (Melander and Qvint 2016).

Bioethanol is a renewable and environmentally friendly source for energy and high-value derivatives. Additionally, bioethanol's catalytic dehydration is a sustainable alternative for bio-ethylene production (Fan *et al*. 2013). Bioethanol dehydration could be a more sustainable and less expensive pathway for bio-ethylene production compared to the oil-based pathway (Becerra *et al*. 2017).

First-generation (1G) bioethanol is produced from sugar-rich and renewable feedstock resources, such as sugarcane, corn grains, potatoes, wheat, cassava, and sugar beet, among other crops (Hettinga *et al*. 2009; Kagyrmanova *et al*. 2011; Haro *et al*. 2013; McKechnie *et al*. 2015; Mohsenzadeh *et al*. 2017; Zacharopoulou and Lemonidou 2017). On the other hand, second-generation (2G) bioethanol may provide an opportunity to develop sustainable biorefineries (Adekunle *et al*. 2016; Vallejos *et al*. 2017; Mendes *et al*. 2020). Compared to gasoline production, bioethanol production has a positive net-energy output (64% to 86%) and can reduce GHG emissions by 11% to 145% (Werpy and Petersen 2004). Due to its added-value and potential market demand, bioethanol is one of the best candidates as a base for biorefinery products (Huang *et al*. 2011; Pérez *et al*. 2020). Second-generation bio-ethylene is made from non-alimentary carbohydrates by the conversion of low-cost agroforestry residues that favor its valorization (Alvarez-Castillo *et al*. 2012). The main routes to convert carbohydrate biomass to bioethanol, bio-ethylene, and polyolefins are displayed in Fig. 1.

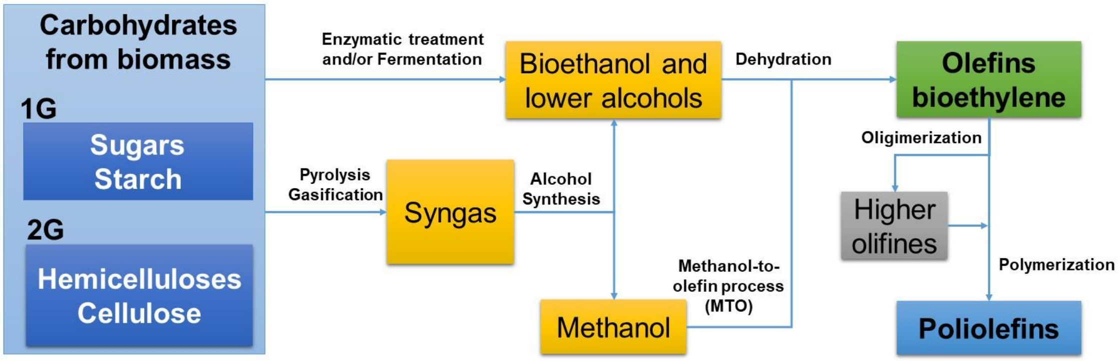

Fig. 1. The production process to make bio-ethylene and polyolefins from carbohydrate biomass (adapted from Grassi *et al.* 2015).

Ethanol is an important industrial commodity, and its chemical potential to generate an ethylene platform is enormous and among the top opportunities from carbohydrate biorefineries. The bio-ethylene from 1G or 2G ethanol is chemically identical to the oil-based one, but it is produced from a different carbon source. Technological improvements are necessary to attain the commercial scale production from 2G ethanol. The high yield catalysts need to be improved and the costs of the feedstocks and processes need to decrease (de Andrade Coutinho *et al*. 2013).

The northeast region of Argentina (NEA) is the largest forested area of the country. The Province of Misiones, with 405,824 ha planted (mostly pines), has an important forest-industrial activity. It accounts for 46% of the country's sawmills, which produce large amounts of lignocellulosic residues (sawdust, bark, others). These lignocellulosic residues create pollution, increase the risks of fire, increase the presence of pests, and the disposal of the residue occupies valuable space (Vallejos *et al*. 2017; Pérez *et al*. 2020). Currently, the concept of biorefinery and biomass residue valorization can add value to the forest-industrial cycle due to the large quantities of waste materials that are rich in sugars, lignin, lipids, and proteins (Area and Vallejos 2012; Area and Park 2017). Agro-industrial and forest industrial lignocellulosic residues are valuable feedstocks for ethylene production from 2G bioethanol.

This work analyzes the stages, possible derivatives, uses, and applications of 2G bio-ethylene production within a biorefinery framework. An extensive bibliographic review was carried out, and the potential replacement of fossil-fuel-based ethylene from 2G bio-ethylene was evaluated. The technical, economic, and environmental implications of the production of ethylene from biomass were established, considering the biomass available in Argentina's NEA region as a case study.

BIO-ETHYLENE MARKET

Ethylene is a highly reactive unsaturated hydrocarbon (alkene), which makes it a potential chemical building block. Ethylene can typically react as a short-chain olefin, from which it can produce mixtures of different compounds during its production process, which should be further separated (Zimmermann and Walzl 2000). Ethylene is primarily used in the transportation, textiles, packaging, and electronics industries, among others (Wiley-VCH 2016). Currently, there is a strong demand for ethylene use in bioplastic production (Martinz and Quadros 2008; Mendieta *et al.* 2019). The ability to close the biorefinery scheme can be valuable to produce derivatives such as bio-polyethylene (bioPE), bio-polyvinyl chloride (bioPVC), bio-polyethylene terephthalate (bioPET), bio- polypropylene (bioPP), and others (Area and Park 2017; Brodin *et al*. 2017). In addition to the production of polymers, bio-ethylene can be used in the chemical industry as an intermediate compound in the synthesis of alcohols, olefins, acetaldehyde (C_2H_4O), ethylbenzene, and vinyl acetate, among others (Zimmermann and Walzl 2000). The industrial processes with high ethylene consumption are the polymerization to low-density polyethylene (LDPE) and high-density polyethylene (HDPE), the chlorination to 1,2-dichloroethane, the oxidation to ethylene oxide (EO), the sequential reaction to form ethylbenzene that is dehydrogenated to styrene, the oxidation process to C_2H_4O, and the hydration reaction to ethanol, among others (Zimmermann and Walzl 2000).

The current annual global production capacity of ethylene is over 140 to 150 million tons (Alonso-Fariñas *et al.* 2018; Oliveira *et al.* 2019). The ethylene market size was approximately $160,000 million USD in 2015 and it is estimated to exceed $235,000 million USD in 2024 (Global Market Insights 2016). The selling price of ethylene fluctuated between 2018 and 2019. It decreased by 15% to 35%, reaching $1,000 USD/t in May 2019 (ICIS 2020), mainly due to the decrease in oil prices (Min-hee 2019; Hall 2020).

There are several polymer derivatives of ethylene that are used in various applications. Polyethylene (PE) is used in packaging, stretch films, containers, drums, pallets, and other applications (Wiley-VCH 2016). Ethylene oxide is used to produce polyester fibers, resins, and polyester films, among others (Graham *et al.* 1989). Polypropylene (PP) is used to produce films, sheets, foamed products, industrial products, reinforced products, and containers, among others (Kikuchi *et al.* 2017). Polyethylene terephthalate (PET) is mainly in the production of soda bottles and many other packaging materials (Spencer 1994). Polyvinyl chloride (PVC) is used to manufacture packaging containers and bottles (Spencer 1994; Wiley-VCH 2016). Polystyrene (PS) is used to produce electronic and electrical equipment (Thakur *et al*. 2018).

Polyethylene accounts for 60% of the global ethylene demand, followed by EO. Both PE and EO are used to make ethylene glycol (ICIS 2010). The common prices for PE derivatives are between $1,100 USD/t and $1,300 USD/t for LDPE (ICIS 2019; Santagata *et al*. 2020) and $1,150 USD/t to $1,400 USD/t for HDPE (ICIS 2019). The reported market prices for ethylene glycol and PP are approximately $0.4 USD/t to $1.4 USD/t and $1,500 USD/t, respectively. (ICIS 2013; Taylor *et al*. 2015; Echemi 2021).

Besides polymer production, ethylene is used in many applications. To give some examples, it is used to control the ripening of fruit, to promote crop growth in agriculture, in the production of specialty glass for the automotive industry, as an anesthetic in medical applications, as a refrigerant, and as oxy-fuel gas in metal works (Keller *et al*. 2013).

The hydrocarbon cracking process to obtain ethylene requires intensive fossil energy use, which has a large environmental impact. Steam cracking might create an economic impediment for further developments of bio-based ethylene production. Nevertheless, research on technologies for the dehydration of ethanol in ethylene continues to advance. On the other hand, small-scale production could be an interesting niche since full-scale crackers (using either naphtha or natural gas) would not be commercially viable. In this sense, bio-ethylene production might be commercially viable due to the possibility of using the current conversion and production equipment, besides the necessity of process optimization. To meet this demand, several companies have researched and patented various technologies for the dehydration of ethanol into ethylene (Chieregato *et al*. 2016). Moreover, there is less need for development of the supply chain and logistics for the provisions of raw materials and inputs (Wyman *et al*. 2017). The current global demand for 1G bio-ethylene market is 127 million tons per year. Approximately 0.2% of this demand (0.25 million tons per year) comes from biomass resources (Kagyrmanova *et al*. 2011; Broeren 2013).

In the polymer field, the non-biodegradable, versatile, and chemically stable bio-PE and bio-PET materials have gained interest in recent years (de Jong *et al*. 2012b; Hottle *et al*. 2013; Iwata 2015; Mendieta *et al*. 2019). Coca-Cola's commercial bottling plant currently utilizes bio-PET (Taylor *et al*. 2015). Toyota also uses bio-PET for the production of the interior surfaces and liner material in their vehicles (de Jong *et al*. 2012a). Bio-polyethylene can substitute petroleum-based PE in several applications (Mendieta *et al*. 2019), so bio-PE may soon become the most widely used bio-based plastic (Taylor *et al*. 2015). Currently, the prices of fossil-fuel-based PE are lower and they can be processed more easily than bio-PE materials (Taylor *et al*. 2015). Therefore, process improvements in the manufacturing of bio-PE and bio-PET are necessary to ensure they can compete with fossil-fuel based plastics.

2G BIOETHANOL PRODUCTION

Ethylene production by 2G bioethanol dehydration, using forest or agro-industrial waste is a sustainable alternative to oil-based one (Santos-Panqueva *et al.* 2017). Gasification of lignocellulosic biomass is a thermochemical route to produce bioethanol. Using chemical catalysts, the synthesis gas generates ethanol together with a mixture of alcohols. Another option to produce ethanol is the fermentation of the synthesis gas (Wagner and Kaltschmitt 2013). Compared with the SHF and SSF routes, gasification has some handicaps. It requires high temperatures, and both the moisture content of the raw material and the contaminants of the synthesis gas must be removed because of their negative impact on the performance of catalysts and fermentation broths. Therefore, the biochemical route is the most efficient one (Silva-Ortiz *et al.* 2020).

The ethylene production process consists of pretreatment, enzymatic hydrolysis, fermentation, recovery by distillation, and dehydration (Yakovleva *et al*. 2016). There are challenges to achieve commercial-scale production by 2G bioethanol dehydration, such as the selection of a suitable treatment of the lignocellulosic biomass to obtain a cellulosic fraction, the conversion process of cellulose to ethanol, and the fermentation selectivity. These processes have direct effects on the bioethanol yield and production cost (Saha 2003; Zhu *et al*. 2011; Broeren 2013). Moreover, efficiency increases if both pentose and hexose are converted in bioethanol (Sharma *et al.* 2020).

The conditions and type of pretreatment depend exclusively on the chemical composition of the feedstock (Kruyeniski *et al*. 2019), which has a significant influence on the enzymatic hydrolysis and following processes (Vallejos *et al*. 2017). For example, coniferous wood for 2G bioethanol production is attractive due to its abundance and high content of hexoses (Area *et al*. 2012; Kruyeniski *et al*. 2017). However, the pretreatment of coniferous wood can be hindered by its high lignin and extractives content and its highly crystalline cellulose (Stoffel 2016).

Before the production of 2G bioethanol, it is critical to pretreat the lignocellulosic biomass. An efficient pretreatment should apply to various substrates using cheap and easily recoverable reagents, with low energy consumption, and low investment and maintenance costs, among other features (Almenares-Verdecía *et al.* 2008). The reactions must favor the formation of sugars, avoid their loss by degradation, and limit the production of inhibitory products (Kumari and Singh 2018). New research should focus on developing new low-cost and environmentally-friendly pretreatment techniques to produce a purified cellulosic material with high yield. The pretreatment process extracts the lignin and hemicellulose in order to increase the porosity of the material to improve cellulose accessibility to the enzymatic attack. The pretreatment process should also limit the degradation of other carbohydrates and, in the saccharification stage, avoid the formation of inhibitor products (Kruyeniski *et al*. 2019).

The cellulose that is obtained from the pretreatment can be transformed into ethanol in two steps. Initially, cellulose is depolymerized to glucose by hydrolysis, and then these sugars are fermented into ethanol (Hahn-Hägerdal *et al*. 2006; Ximenes *et al*. 2011; Gu *et al*. 2014). Depending on the strains, the optimum temperature for the development of fermentation yeasts is usually between 25 °C to 35 °C (Palmqvist and Hahn-Hägerdal 2000). *Saccharomyces cerevisiae* is the most common yeast for industrial production because of its capability to efficiently ferment glucose and other hexoses to bioethanol. *S. cerevisiae* can withstand temperatures up to 38 °C, but the fermentation performance decreases noticeably (Azhar *et al*. 2017). The high-temperature fermentation process is beneficial because it uses heat-tolerant microorganisms that do not incur cooling costs (Fonseca *et al*. 2008). Some microorganisms can withstand high temperatures. For example, *Kluyveromyces marxianus* is a thermotolerant yeast that can survive at 42 °C to 45 °C, with the capacity to ferment both hexoses and pentoses (Yanase *et al*. 2010). The common pretreatment strategies of separate hydrolysis and fermentation (SHF) and simultaneous hydrolysis and fermentation (SSF) (Balat 2011) are shown in Fig. 2.

In the SHF process, cellulose hydrolysis and glucose fermentation are accomplished separately, which allows each stage to occur at its optimum conditions. However, the separate conditions are disadvantageous for the generation of inhibition products, such as glucose for hydrolysis and ethanol for fermentation (Araque *et al*. 2008; Kruyeniski 2017). On the other hand, the SSF process requires only one reactor for hydrolysis and fermentation. The SSF process is advantageous because the sugar monomers that are released during the saccharification process are immediately fermented by the microorganisms, which decreases the risk of microbial contamination (Area *et al*. 2012; von Schenck *et al*. 2013). Glucose is instantly fermented into ethanol (Becerra *et al*. 2017), regardless of the optimum temperature and the pH parameters for the hydrolysis and fermentation processes. Therefore, the SSF process is the most feasible and cost-effective alternative to produce bioethanol considering the low generation of inhibitory products and the utilization of only one fermenter in the whole process, which reduces the investment costs (Wingren *et al*. 2003; Arismendy *et al*. 2018; Olofsson *et al*. 2008). Table 1 shows some examples of bioethanol yields using the SHF and SSF strategies.

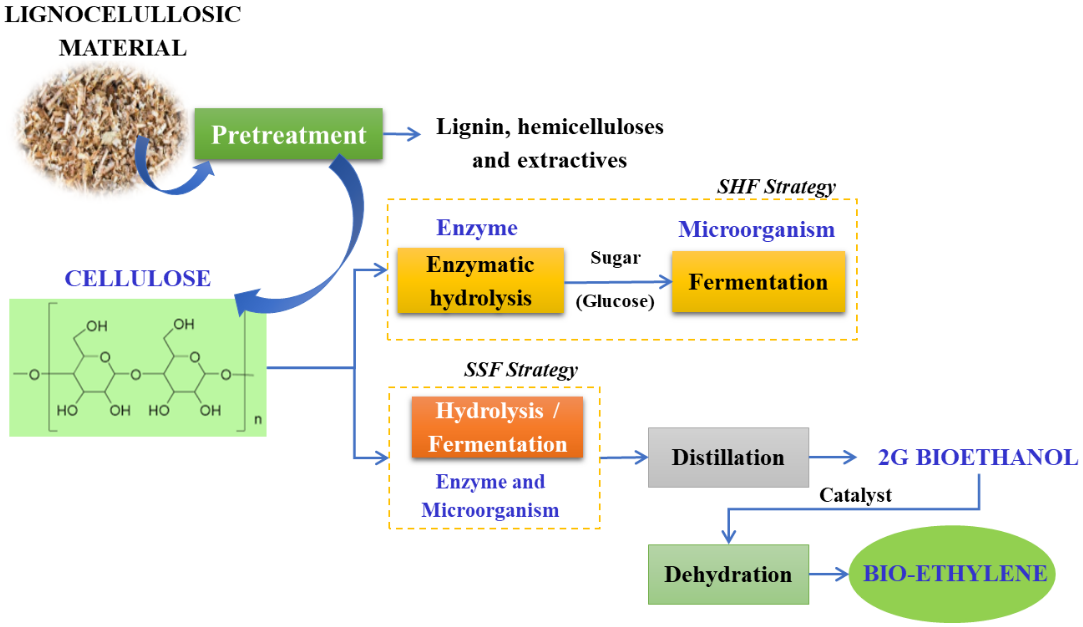

Fig. 2. The sequences of the 2G bio-ethylene production by the SHF and SSF strategies

Table 1. Various Bioethanol Yield (BEY) Values Obtained from SHF and SSF Strategies from Softwoods

Raw Material	Origin	Strategy	BEY (%)	Conditions	Scale	Reference
Pinus pinaster Stumps	Portugal	SSF	97%	15 (FPU)/g pulp Cellic® Ctec*2* (CTec2), 72 h, 38 °C *S. cerevisiae*	250 mL Erlenmeyer flasks, 50 mL working volume	(Mendes *et al*. 2020)
Pinewood chips	Italy	SHF	96.1%	CTec2, 48 h, 50 °C *S. cerevisiae*, 48 h, 32 °C	Bioreactor of 6 L capacity	(Cotana *et al*. 2014)
Softwood kraft unbleached pulp	Japan	SSF	62.8%	15 (FPU)/g pulp *EPEG-SL*, 72 h, 38 °C *S. cerevisiae*	100 mL scale fed-batch	(Cheng *et al*. 2017)
Pinus radiata	Chile	SSF	95%	0.44 g of Cellic® Ctec3 (Ctec3)/g of dry substrate, 72 h, 40 °C *Saccharomyces* IR2-9	Not specified	(Valenzuela *et al*. 2016)
Pinus sylvestris	Finland	SSF	87.8%	10 (FPU)/g pulp Celluclast® *1.5 L* and Novozyme188 (200 nkat/g dry matter). 72 h, 40 °C *S. cerevisiae* IR2-9	250 mL Erlenmeyer flasks, 100 mL working volume	(von Schenck *et al*. 2013)
Pine waste	Argen-tina	SHF	83%	*Trichoderma reseei* (20 FPU/g glucans), 48 h, 50 °C *S. cerevisiae*, 48 h, 30 °C	50 mL Erlenmeyer flasks	(Kruyeniski 2017)

High bioethanol yields are justified by low lignin content in the substrate (pretreated pulp), because of its low toxicity for both yeasts and enzymes (von Schenck *et al.* 2013). Mendes *et al*. (2020) reported ethanol yields of about 97% in the SSF strategy, using *Pinus pinaster* stumps. This was higher than that obtained by Cheng *et al.* (2017) (62.8%) in the same conditions (72 h, 38 °C, and enzyme charge).

Several fungi and bacteria for the hydrolysis of lignocellulosic biomass were studied to evaluate the possibility of producing ethylene at a commercial level. However, it was discarded because the obtained yields of ethylene were significantly low using wild yeasts (*Penicillium digitatum* and *Pseudomonas syringae*). Studies that utilized enzymes at the laboratory scale resulted in negligible ethylene yields, which illustrates that this process is not commercially applicable (Manikandan *et al*. 2016).

BIO-ETHYLENE PRODUCTION FROM 2G BIOETHANOL

In the petrochemical industry, dehydration of ethanol to ethylene is a usual process (Kniel *et al*. 1980). Nevertheless, for the ethylene process, ethanol purity must be higher than 95 wt%. Besides, bioethanol has particularities that make necessary further treatment previous to ethylene processing. Unlike ethanol, both 1G and 2G bioethanol come from a fermentation broth that contains microorganisms, nutrients, and reaction by-products. The obtained bioethanol must be purified by removing contaminants and additional water. For this, several methods combine distillation, adsorption, extraction, among others, such as separation by membrane pervaporation (Feng and Huang 1997), extractive distillation (Mendoza- Pedroza *et al*. 2018), or heteroazeotropic distillation (Frolkova and Raeva 2010), which have been exhaustively described in the literature. For ethylene production, in particular, Very High Gravity (VHG) fermentation emerges as an interesting option to explore and optimize when using SHF, since it can improve fermentation performance and purify ethanol simultaneously (Kang *et al*. 2014b). Considering that this is a stage of great energy consumption (Cardona *et al*. 2006), it is one of the steps that require optimization to contribute to the economic viability of bio-ethylene.

Lignocellulosic biomass as a substrate could also contain reaction products from pretreatments, such as furfural and acetic acid, which could become bioethanol contaminant by carryover. However, a simulation carried out with the Aspen program showed that the impurity profile of ethanol feed does not have a significant effect on the quality of the obtained bio-ethylene (Mohsenzadeh *et al*. 2017). Experiences are needed to corroborate this supposition.

The process to manufacture bio-ethylene involves an endothermic reaction that occurs under adequate temperature and with the aid of a catalyst (Mohsenzadeh *et al.* 2017). The type of catalyst and the process conditions determine the extent of the side reactions. For example, the dehydrogenation of ethanol can produce C_2H_4O and hydrogen gas (H_2). Ethylene can be dimerized and oligomerized to C4 olefins, which can be hydrogenated to saturated hydrocarbons (mainly ethane). Other reactions involve impurities in the feedstock, such as the dehydration of heavier alcohols. A variety of reaction byproducts can be found in ethanol dehydration, including acetic acid, ethyl acetate, acetone, methanol, short hydrocarbons (methane, ethane, propane, propylene, others), CO, and CO_2, among others. These compounds impact the separation process and recovery costs.

Ethylene is formed by the highly endothermic intramolecular dehydration of ethanol, which eliminates one oxygen atom and two hydrogen atoms. The formation of ethylene occurs at temperatures between 350 °C and 500 °C, which promotes the use of adiabatic reactors because they provide suitable temperature sets and low investment costs (Kagyrmanova *et al*. 2011; Nitzsche *et al*. 2016). At low temperatures, intermolecular dehydration also produces diethyl ether, which can be sequentially dehydrated to form ethylene. Therefore, controlling these side reactions could reduce the costs associated with the removal of by-products (de Andrade Coutinho *et al*. 2013).

Ethylene production from lignocellulosic biomass at the industrial level requires processes that attain the theoretical yield of 2 ethylene mol/glucose mol or 0.31 g/g by glucose fermentation to ethanol and subsequent acid-catalyzed ethanol dehydration to ethylene. Ideally, 1 mol of glucose can be converted to 2 mol of ethylene produced from ethanol, using enzymes for dehydration together with ethanol-producing microorganisms. However, more studies on the equilibrium of the dehydration reaction and the fermentation conditions are required to determine the technical feasibility of this process (Endres 2017; Pardo *et al*. 2018).

In brief, the process to obtain marketable polymer-grade ethylene involves several stages. First, the concentrated ethanol must be pressurized at 1.14 MPa. Next, the feed stream must be preheated using the hot exhaust gas from the adiabatic reactor, after which it is cooled to 84 °C. The water in the gas stream at the top of a rapid cooling tower is then condensed at 1 MPa. The solution is cooled to 20 °C, and a fraction of the bottom liquid is recirculated. Next, the dry gas is compressed to 2.7 MPa in a three-stage compressor, removing the condensed water from each stage of the compressor. The CO_2 is absorbed in a packed column, washed with NaOH, and the gas is washed with a water spray at the top of the column to remove the NaOH. The remaining water is then extracted in the ethylene-rich gas with a molecular sieve. Finally, the gas is cooled to saturation and cryogenic distillation (84 stages and a pressure drop of 0.25 MPa, 75% efficiency) to remove the heavier impurities.

The heaviest hydrocarbons are removed in the bottom flow, and the top product is ethylene, with a 99.1% recovery rate. The CO, CH_4, and H_2 are removed with a 75% efficiency from ethylene in a 20-stage downstream stripper with a 0.25 MPa pressure drop. The bottom product is polymeric ethylene. The overhead compounds are pressurized and partially condensed, while the low molecular weight compounds are vented, and the condensed ethylene is returned to the separator (Morschbacker 2009; Nitzsche *et al*. 2016).

For the dehydration reaction, catalysts are necessary (Fan *et al*. 2013). Many laboratories are developing synthesized catalysts to achieve better ethanol conversion and ethylene selectivity rates (Wu and Wu 2017). These should soon allow the profitability of large-scale bio-ethylene production (Kagyrmanova *et al*. 2011) compared to steam cracking plants (Fan *et al*. 2013). The different catalysts that have been tested and developed to produce bio-ethylene are shown in Table 2. Alumina or alumina in conjunction with metal oxides as promoters, silica, clay, several metal oxides, phosphorus oxides, phosphates, molybdates, sulfuric acid, and zeolites, among others, have been studied as catalysts. Industrially, phosphoric acid and alumina have been used on a small-scale and they have been used to increase the ethylene selectivity (de Andrade Coutinho *et al*. 2013).

Table 2. Catalysts Tested for the Ethanol Dehydration Reaction to Produce Ethylene

Catalyst	Max. Ethylene Selectivity (%)	Ethanol Conversion (%)	Reaction Temperature (°C)	Stability	Reference
Zeolite HZSM-5 modified with 0.5%-La-2% P	99.9	100	240 to 280	High	(Hu *et al*. 2010)
Si/Al	99.0	100	500	High	(Rossetti *et al.* 2017)
Ƴ-Al_2O_3	80	100		Stable	
HZSM-5	98.8	99.0	250	High	(Sheng *et al*. 2013)
HT400	98.9	99	260		
HT500	98.5	98.6	275		
HT550	98.2	94.9	290		
La-modified HZSM-5 zeolite	98.5	99.5	260	High	(Ouyang *et a*l. 2009)
Phosphorus (P) modified H-ZSM-5	98	99	450	High	(Ramesh et al. 2010)
Al_2O_3	97.7	99.8	> 400	High	(Tripodi *et al.* 2019)
Al_2O_3	97	99	450	High	(Kagyrmanova *et al*. 2011)
HZSM-5 zeolite	90	90	245-260	Stable	(Moon *et al.* 2019)
Al_2O_3	82.8	90.1	350 to 475	Stable	(Zhang *et al*. 2008)
HZSM-5	93.1	97.3			
SAPO-34	86.0	93.5			
NiAPSO-34	92.3	96.5			
Zeolite ZSM-5	80	99	400	Low	(Wu and Wu 2017)
	72	42	300		

Kagyrmanova *et al.* (2011) reported maximal ethylene selectivity when the concentration of ethanol in the feedstock was above 94 wt% between 370 °C and 400 °C. Ouyang *et al.* (2009) achieved a maximum ethylene selectivity of 98.5% and an ethanol conversion rate of 99.5%, which indicated that higher temperatures favored the dehydration reaction of ethanol and the yield of ethylene.

Alumina is the most commonly used catalyst for the dehydration of bioethanol, as it can withstand temperatures above 450 °C, but it deactivates quickly at temperatures below 300 °C. Zeolites are used to carry out the reaction because they do not require high temperatures, but at low-temperatures coke formation can produce the catalyst deactivation (de Andrade Coutinho *et al*. 2013). For example, Sheng *et al*. (2013) reported maximum ethylene selectivity and ethanol conversion rates of 98.8% and 99%, respectively, when HZSM-5 was used as a catalyst at a temperature of 250 °C.

The effluents contain a high amount of water from the dehydration reaction, as well as ethanol feedstock and heat-carrying fluid. Water can be separated in a quench tower, and the residual ethanol and water-soluble oxygenates can be re-heated and distilled. The residual ethanol and diethyl ether (low water solubility) can be recovered and recycled to the feedstock, while the C_2H_4O can be burned in the furnace. The gas from the top of the quench tower primarily contains ethylene (90% to 99.5%), hydrocarbons, H_2, CO, CO_2, and oxygenates. The ethylene can be washed with cool water in a second tower removes the oxygenates, and caustic washing can remove CO_2 and acids (de Andrade Coutinho *et al*. 2013).

CONSIDERATIONS IN THE USE OF LIGNOCELLULOSIC BIOMASS FOR ETHYLENE PRODUCTION

Technical Considerations

In a biorefinery platform for ethylene production from biomass, either by biochemical or thermochemical pathways (Alonso-Fariñas *et al.* 2018), the high energy consumption could lead to high production costs. Several ethylene production processes have been developed and analyzed. Hackl *et al.* (2011) found that when one refinery was used for the bio-ethylene production process, the heat utility demand of the ethanol and the ethylene plants decreased from 131 MW to less than 80 MW. In a combined biorefinery, the flue gas can be integrated with the ethanol dehydration reactors, which will further reduce the utility demands (Hackl *et al.* 2011).

In the biochemical process, the pretreatment and ethanol recovery stages consume a large amount of energy (Hackl *et al.* 2011; Nitzsche *et al*. 2016). The complexity of wood as raw material directly affects the integration mechanism (Mendieta *et al*. 2019) and the pretreatment cost (Rosales-Calderon and Arantes 2019). Energy integration strategies could be applied in these processes, with theoretical savings for heat demand of 31.5% (15.1 MW) and cooling demand of 39.5% (13.8 MW) (Nitzsche *et al*. 2016; Becerra *et al*. 2017). Generally, the production of ethanol requires a large amount of energy. Among the strategies developed to make it cost-effective (Ferreira *et al*. 2018; Ayodele *et al*. 2020), the most important are heat, energy, and mass integration (Cardona and Sánchez 2007; Clauser *et al*. 2021).

Among the different alternatives mentioned to integration, the most promising replaces the improvement of the individual sectors with a systemic approach, with a full scope of the process. In this way, it is possible to control the effect of the optimization proposed in each of the stages (Hackl and Harvey 2016; Valderrama *et al.* 2020). In this sense, it is possible to take advantage of the high heat content in the different stages, as the condensation in the ethanol purification at the output of ethylene reactors. Besides, the heat available in the cooling of the hydrolysis and fermentation processes can be leveraged in the ethanol production process, for example, in the pretreatment stage (Alonso-Fariñas *et al*. 2018). Nowadays, the facilities that use cogeneration and have residual heat can sell the excess. However, the profit of heat exchange reduces their advantages when ethanol production and dehydration to bio-ethylene processes are located in different locations (Hackl and Harvey 2016).

Some of the improvements obtained through process integration are summarized in Table 3. Moreover, the high investment costs for development at the industrial scale should be taken into consideration. There are complicated factors to consider in the decision-making process, such as the raw material, the pretreatment methods, the production costs, the production scale, and the yield, among others (Kang *et al*. 2014a; Brown 2015; de Assis *et al*. 2017; Meneses 2018). In order to attain competitive production costs, it is necessary to improve other key factors such as the development of new low-cost conversion strategies. Such strategies may include reducing the consumption of enzymes, reagents, and water, among others, in addition to new strategic policies for bio-based products. The production of derivatives and new products must be developed for the emerging bio-based markets (Mohsenzadeh *et al*. 2017; Tripodi *et al*. 2019). Biopolyethylene, which can be replaced in various uses by degradable bioplastics, is still essential in some medical and industrial applications. So, the processing of this classical derivative, and also of bio-PET, must also be improved.

Table 3. Integration Strategies for Ethanol and Ethylene Production

Feedstock	Strategy	Improvement	Ref
Sugarcane	EI	Energy reduction of 50% compared with no energy integration.	(Oliveira *et al.* 2016)
Sugarcane	EI	With the integrated heat exchanger networks (HEN) it is possible to reach more than 70% of process steam reduction with energy integration.	(Oliveira *et al*. 2018)
Beechwood	EI	The demand for total energy was reduced by more than 32%.	(Nitzsche *et al.* 2016)
Molasses and sugarcane bagasse	EI, MI	53% reduction of heat exchange units and 19.25% reduction of the cost of industrial cooling services. 16.53% reduction of the process freshwater consumption.	(Valderrama *et al*. 2020)
Sugarcane bagasse	EI, MI	Potential reduction in steam consumption by almost 35%.	(Dias *et al*. 2011)
Corn stover	EI*	Up to 47.6% savings of the total annual costs.	(Nhien *et al*. 2017)

EI: Energy integration; MI: Mass integration. *Energy integration and intensification.

While the development of a biorefinery plant presents some challenges, it does offer some considerable advantages (Fig. 3).

Fig. 3. The advantages of converting wood waste product to bio-ethylene

Economic Considerations

The reported selling price of 1G bio-ethylene is approximately $1,100 to $1,500 USD/t (Budzinski and Nitzsche 2016; Nitzsche *et al.* 2016; Alonso-Fariñas *et al*. 2018; Jiang *et al*. 2019), but in some cases it may reach higher than $2,000 USD/t (Taylor *et al*. 2015). According to recent investment information, the capital costs for bio-ethylene production, depending on the process, could range from $460 USD/t (Becerra *et al*. 2017), between $1,100 and $1,400 USD/t (Broeren 2013), $3,880 USD/t (Nitzsche *et al*. 2016), and $5,750 USD/t of ethylene per year (Budzinski and Nitzsche 2016). Some of the production costs are presented in Table 4.

Table 4. Ethylene Production Costs as Reported by Several Studies

Raw Material	Capacity (ton of ethylene/ year)	Year	Production Cost (USD/t)	Country	Ref
Beech wood	400,000[a]	2016	1,349[b]	Germany	(Nitzsche *et al.* 2016)
Corn[b]	-	2009	2,060	USA	(Broeren 2013)
Sugarcane	-	2009	1,190	Brazil	(Broeren 2013)
Sugarcane	-	2009	1,220	India	(Broeren 2013)
Sugar beets	-	2009	2,570	Europe Union	(Broeren 2013)
Sweet sorghum	-	2009	1,650	China	(Broeren 2013)
Sugarcane bagasse	500,000	2019	1,006 to 1,436	Brazil	(Oliveira *et al.* 2019)
Spruce – Salix – Corn stover	200,000	2011	1,012 to 1,084[c]	Sweden	(Hackl *et al.* 2011)
Sugarcane	1,000,000	2012	1,347	Brazil	(Cameron *et al.* 2012)
Corn	9.9 to 38.9[d]	2013	1,724 to 1,762[c]	Europe Union	(Haro *et al.* 2013)
Biomass	9.9 to 38.9[d]	2013	1,219 to 1,182[c]	USA	(Haro et *al.* 2013)
Sugarcane	9.9 to 38.9[d]	2013	1,053 to 1,016[c]	Brazil	(Haro *et al.* 2013)

[a]Raw material per year. [b]Minimum selling price in €. [c]Values in €. [d]t/h.

The prices and production costs of bio-ethylene are similar to those of oil-derived ethylene (Nitzsche *et al*. 2016; Santagata *et al*. 2020). However, the market price of bio-ethylene derivates, such as polymers, is slightly higher than the market price of oil-derived ones (Taylor *et al.* 2015). Some researchers have reported a 30% to 60% premium in the price of bio-PE (Taylor *et al.* 2015; Nitzsche *et al.* 2016). Similarly, the price of bio-PET is not competitive with the usual price of PET (Taylor *et al.* 2015). However, the biorefinery concept looks very promising when considering the willingness of consumers to pay a higher price for biopolymers and bio-ethylene (Nitzsche *et al.* 2016).

Sensitivity assessments developed for bio-ethylene production using sugarcane and beech wood as raw materials showed a strong dependence on the price of the raw material (Nitzsche *et al*. 2016; Oliveira *et al.* 2019) and the selling prices of the products (Nitzsche *et al.* 2016). In these works, the cost of the raw material was important (more than $100 USD/t in some cases). However, in developing countries, the costs of the feedstock and labor are lower than in developed countries, so bio-ethylene production may be an attractive alternative to add value to lignocellulosic wastes. For example, the raw material may comprise 60% to 75% of the production costs depending mainly on the final product (biomass or ethanol) and the geographic region, but in regions where the feedstock and labor are cheaper, like Brazil, India, and Argentina, the production costs could be reduced (Mohsenzadeh *et al.* 2017).

Currently, mills like Braskem in Brazil (Broeren 2013; Oliveira *et al.* 2019), India Glycols Limited in India (Global Market Insights, 2016), and Greencol Taiwan Corporation in Taiwan (Chemicals-Technology 2020), produce 1G ethylene from sugarcane and molasses, with annual capacities between 100 and 200 kt. There are also projects in a developing stage like Dow/Mitsui in Brazil from sugarcane (with a project capacity of 300 kt/year) (Moser 2013). There are reports of several plants in China with annual capacities between 9 kt and 80 kt, but their status is unknown (Broeren 2013).

Environmental Considerations

Compared to fossil-fuel based ethylene, the production of bio-ethylene has great potential to reduce environmental impacts. However, new developments in the conversion and recovery processes are necessary to make commercial-scale production of bio-ethylene feasible. Some global progress has been made to make this a reality. In 2015, 17 sustainable development goals were listed by world leaders that sought to delay climate change, including improvements in sustainable energy generation, industry and innovation, responsible consumption, and sustainable use of biodiversity (Organización de las Naciones Unidas 2015; Mestre 2018). All these concepts align with the biorefinery schemes adapted to the circular bioeconomy (Näyhä 2012; Cristóbal *et al*. 2016). However, the bioeconomy amounts to only 11% of the economy of the European Union and 5% of that of the USA (Kuosmanen *et al.* 2020; The National Academies of Science, Engineering, and Medicine 2020).

There are few studies on the life cycle assessment (LCA) of chemicals derived from biomass (Alonso-Fariñas *et al.* 2018). For bioethanol production, base-product of 2G bio-ethylene, studies have shown a clear reduction in GHG emissions and ozone layer depletion (Morales *et al.* 2015).

Compared to bio-ethylene, fossil-based ethylene production greatly contributes to global warming and photochemical ozone creation (Liptow *et al.* 2015). Carbon dioxide emissions can be reduced by approximately 2.5 tons per ton of produced bio-ethylene if fossil-fuel based chemicals are replaced by biobased ones (de Jong *et al.* 2012a).

A LCA compared thermochemical and biochemical processes for bio-ethylene production from sugar beets, considering 11 potential impacts (Liptow *et al.* 2015). The LCA showed that the gasification pathway has a lower impact than the fermentation route. The bio-chemical option had a lower impact on human toxicity, freshwater aquatic ecotoxicity, and terrestrial ecotoxicity potential than the thermo-chemical route. For the remaining eight impacts, the thermochemical option was more sustainable (Alonso-Fariñas *et al.* 2018). Compared with fossil-fuel based PE, bio-PE can reduce environmental emissions (Ita-Nagy *et al*. 2020). Sugarcane-based bio-PE can reduce GHG emissions by more than 50% (Taylor *et al.* 2015). However, biomass conversion by both the fermentation and gasification processes should be further analyzed. Various GHG emission savings were reported for the different derivatives of bio-ethylene.

Achieving the commercial-scale development of biorefinery processes requires the involvement of private entities (producers and industry), state organizations (such as universities), and society (Wierny *et al.* 2015; Nguyen *et al.* 2020). Additionally, the laws that guarantee the regulatory framework must be approved (Mestre 2018), and the establishment of the LCA of both fossil-fuel based and bio-based products and materials must be encouraged (Nguyen *et al.* 2020).

Availability of Raw Materials

The productive characteristics of Latin America determine the development of biorefineries (Wierny *et al.* 2015). In 2017, the bioeconomy sector accounted for approximately 16% of Argentina's gross domestic product (GDP) (Coremberg 2018). To increase the impact of bio-based products in the global economy, key factors such as government policies and intersectoral cooperation, among others, must be promoted in the country (Nizami *et al.* 2017).

In Argentina, approximately 50% of the wood from sawmill production, pruning, thinning, and logging is discarded as waste. If an industrial strategy is developed to utilize this wood waste, it can be capitalized for other uses (Uasuf and Hilber 2012; de Assis *et al.* 2017; Clauser 2019; Körte *et al.* 2019). The forestry industry is the primary economic activity in the northeast region of Argentina (Area and Park 2017). Sawmills and lumber mills generate approximately 2.35 million dry tons of wood waste per year, most of which is slash pine and loblolly pine sawdust (Laharrague 2018). In the northeast region of Argentina, forest waste (without urban pruning) amounts to approximately 16 million tons per year (Peirano *et al.* 2019).

Table 5. Recent Studies Carried out in Argentina Oriented to Obtain 2G Bioethanol

Raw Materials	Province	Process	Conditions	Scale	References
Pine sawdust	Misiones	Organosolv pretreatment SSF Strategy	EtOH/NaOH; 1 h, 170 °C *T. reesei* (20 FPU/g glucans); 48 h, 50 °C *S. cerevisiae*; 72 h, 30 °C	Reactor of 200 mL, 100 mL working volume	(Kruyeniski 2017)
Pine sawdust	Misiones	SHF/SSF Strategy	Cellic® Ctec2 *S. cerevisiae,* 72 h, 37 °C	250 mL Erlenmeyer flasks, 100 mL working volume	(Mendieta 2020)
Pine sawdust	Misiones	Pretreatment (Acid and alkaline) Enzymatic hydrolysis	H_2SO_4; 1 h, 121 °C NaOH; 1 h, 121 °C *Celluclast*® 1.5 L (Sigma) 96 h, 50 °C	100 mL Erlenmeyer flasks, 50 mL working volume	(Rodríguez *et al.* 2017)
Rice husks	Chaco	Pretreatment Enzymatic	NaOH; 1 h, 121 ºC *Ctec2* (30 FPU/g glucans,	250 mL Erlenmeyer flasks, 200 mL working	(Arismendy *et al.* 2019)

		hydrolysis and fermentation	*S. Cerevisiae,* 72 h, 37 °C	volume	
Rice husks	Chaco	Pretreatment SHF/SSF Strategy	NaOH; 1 h, 121 °C *Ctec2* (30 FPU/g glucans), *S. cerevisiae,* 72 h, 37 °C	250 mL Erlenmeyer flasks, 100 mL working volume	(Arismendy *et al.* 2020)
White grape marc	Mendoza	Acid pretreatment Saccharification and fermentation	H_2SO_4 (diluted); 1 h, 97 °C Ultrazym Premium DX enzyme; 20 h, 45 °C *S. cerevisiae*; 20 h, 28 °C	500 mL Erlenmeyer flasks, 350 mL working volume	(Díaz 2018)
Sawdust black carob	Chaco	Organosolv pretreatment Acid hydrolysis	NaOH-EtOH-H_2O; 1 h, 121 ºC H_2SO_4; 1 h, 121 °C	Reactor AISI 316, 180 mL working volume	(Dagnino *et al.* 2018)
Sugarcane	Tucumán	Alkaline pretreatment SSF Strategy	NaOH; 1 h, 121 °C Ctec2 and Cellic® Htec2, *S. cerevisiae* 72 h, 35 °C	100 mL Erlenmeyer flasks, 30 mL working volume	(Manfredi *et al.* 2018)
Eucalyptus globulus	Santa Fe	Steam Explosion, Dilute sulfuric acid	H_2SO_4; 1 h, 173 and 216 °C H_2SO_4; 1 h, 120 and 140 °C	Not specified	(Vargas and Vecchietti 2018)
Melon residues	San Juan	Acid pretreatment Enzymatic hydrolysis Fermentation	H_2SO_4 (diluted); 1 h, 55 °C *T. reesei* (20 FPU/g pulp) ATCC26921; 24 h, 45 °C *S. cerevisiae*; 72 h, 35 °C	1000 mL Erlenmeyer flasks, 700 mL working volume	(Montoro *et al.* 2020)
Wheat straw and barley straw	Buenos Aires	SSF Strategy	Ctec2 (20 FPU/g pulp) *S. cerevisiae* 72 h, 30 °C	100 mL Erlenmeyer flasks	(Campos 2018)

Typically, these wood residues are used in boilers and, in the case of pulp and paper mills, are used for steam generation and electrical energy production (Arauco 2020). Some companies produce market chips and pellets destined for Brazil and Uruguay (GP Energy 2020). Various wood residues have different low-value uses in each province. For example, bags of pet products from wood residues, without compacting (Noticias 2010; PinoPack 2020), filler for bricks, firewood (Petri *et al.* 2016), and landfills (Petri *et al.* 2018), are sold in Misiones, Formosa, and Chaco, respectively. No references for obtaining bio-ethylene from biomass in Argentina were found. Several studies were conducted to obtain 2G ethanol in conditions that can be used to produce bio-ethylene (Table 5).

Among the parameters requiring optimization to increase yields, the time of the fermentation stage is a key factor for the subsequent processing steps. For example, (Arismendy *et al.* 2019) obtained the highest production of hydrolyzed sugars at 13 h in the enzymatic hydrolysis stage, (Díaz 2018) at 20 h, and (Montoro *et al.* 2020) at 24 h. The chosen pretreatment is another key factor. For example, the alkaline pretreatments are the most used because they favor the subsequent saccharification of cellulose. Temperature is also an important factor that must be taken into account so that the microorganisms used can carry out their work; for example (Mendieta 2020) and (Pabón *et al.* 2020) used the SSF strategy employing a temperature of 37 °C, being a temperature higher than that used in traditional fermentations. However, Manfredi *et al.* (2018) and Campos (2018) used temperatures of 35 °C and 30 °C, respectively.

Numerous studies state the relevance of using lignocellulosic residues available in the region. Even if potential uses are identified, they are not currently developed.

CONCLUDING STATEMENTS

1. This review has shown that bio-ethylene production from 2G ethanol could have the potential to compete with fossil-fuel-based ethylene when some stages of the whole process are optimized.
2. Biopolyethylene production is the more classical bio-ethylene market, but other significant markets are the control of the ripening of fruit, and the development of the crop growth in agriculture. Biopolyethylene also can be considered for the production of specialty glass for the automotive industry, as an anesthetic in medical applications, as a refrigerant, and as oxy-fuel gas in metal works.
3. The production of bio-ethylene from 2G ethanol is an attractive alternative for regions with low-cost raw materials, such as the northeast region of Argentina.
4. Different mass and energy integration strategies could be employed to substantially reduce production costs.
5. The optimization required to obtain competitive costs includes reducing the consumption of enzymes, reagents, energy, and water, finding more efficient catalysts and purification techniques, and developing new strategic policies for bio-based products, among others.
6. The production of bio-ethylene can reduce environmental concerns such as GHG emissions and the depletion of fossil-fuels. Therefore, more research and development in the conversion and recovery processes for bio-ethylene production are necessary.

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