Chapter

Ethanol Production, Current Facts, Future Scenarios, and Techno-Economic Assessment of Different Biorefinery Configurations

Jesús David Coral Medina and Antonio Irineudo Magalhaes Jr

Abstract

Currently, the continuous depletion of non-renewable resources of fuels and chemicals has promoted the research and development of different alternatives for the replacement of fossil resources as the feedstock of fuels and chemicals. At present, one of the most important biofuels in the current economy, is bioethanol, contributing to 65% of the total biofuels production. The production of bioethanol is an attractive alternative because it would be produced using indigenous and native raw material, therefore, the socioeconomic impact mainly in developing countries would be measured by the economic incomes and increase the quality of life of small and middle farmers. The first-generation ethanol production from sugarcane, corn, or beet sugar is broadly implemented at an industrial scale. However, the second-generation ethanol (2GE) is currently still in development stages, looking for different alternatives according to each region under study. The 2GE is also subject of diverse opinions about its economic viability and its real impact on the environment, especially due to the CO_2 footprint. Consequently, this chapter has presented an overview of 2GE production, the possibilities of co-production of molecules of high value-added, and their economic and environmental assessment, including CO2 release, water consumption, solid residues disposal, and economic analysis to determine the best bioethanol based biorefinery configuration.

Keywords: biorefineries, bioethanol, ethanol controversy, techno-economic assessment, environment impact

1. Introduction

At present the countries, mainly developed, are focused on energy and food security, this phenomenon has emerged in parallel with the reduction in fossil fuels. The continuous increase in the demand for fuels and food has motivated the research to new sources. The production of biofuels and bioenergy using crops or lignocellulosic material as feedstock is an emerging tendency. Bioethanol is the most critical biofuel in the current economy contributing with 65% to global biofuel production, it can play an essential role in the energy and economic security of developed and developing nations if it is produced from native biomass [1, 2].

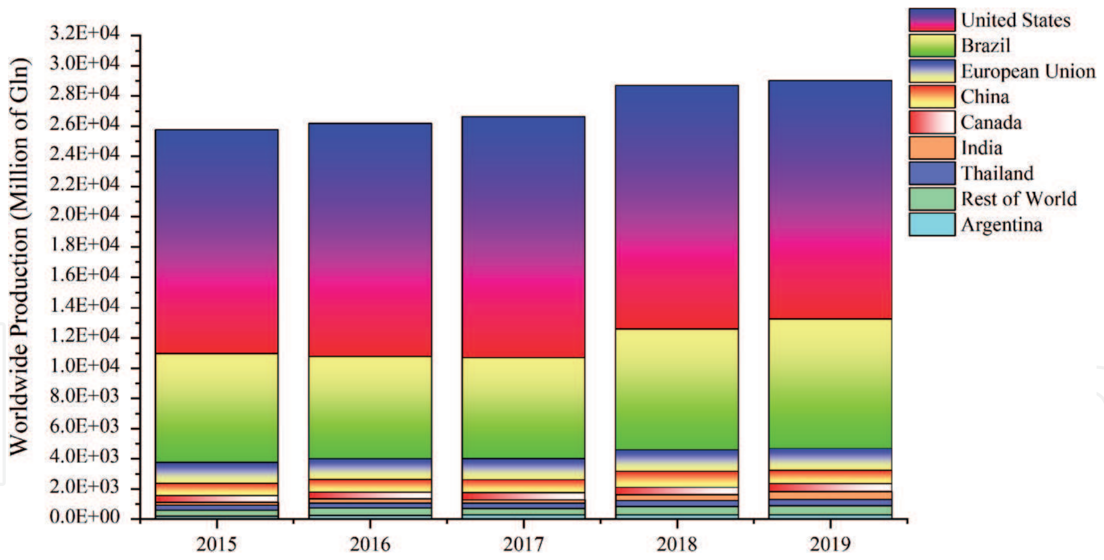

Figure 1.
Worldwide production of ethanol. Data source: https://afdc.energy.gov/data/ [5].

United States of America and Brazil leads the global ethanol production, together they produce a little more than 80% of the alcohol that is used and commercialized in the world. **Figure 1** shows the main ethanol producers in the world in millions of gallons: The United States of America, Brazil, followed by the European Union (EU), China, and Canada. In the United States ethanol is made primarily from corn, while in Brazil is produced from sugarcane. Ethanol production in the EU is exciting because even though the EU is composed of countries with high levels of technological development, the production is less than the United States and Brazil, it is probably because of the lack of standardization of feedstock. In 2014, according to the European Renewable Ethanol Report, the most widely used feedstocks to produce ethanol in Europe were corn, wheat, and sugar beet, which represent about 42, 33, and 18%, respectively [3, 4].

The production of ethanol coming from lignocellulosic material, its mean, any solid waste obtained from agro-industry, is still under study and it is subject to controversy, mainly from the technical and economic view. However, the uses of solid residues have proven to be an alternative for reducing competition for land and water available between crops for energy and food purposes [6].

This chapter has presented the status and tendencies of ethanol production using crops and lignocellulosic material, addressing environmental and economic aspects of the process, as well as future scenarios.

2. Chemistry and types of bioethanol sources

Ethanol is a relatively small chemical molecule, composed of two atoms of carbon, six hydrogens, and one oxygen, its chemical structure is C_2H_6O or C_2H_5OH to highlight the presence of the OH group. The presence of OH groups makes the ethanol a polar molecule. Moreover, the reactivity of the hydroxyl group permits its ready conversion into industrially significant products and intermediates via dehydration, dehydrogenation, condensation, etherification, and/or oxidation reactions [7].

The synthesis of ethanol can be performed both by chemical and microbiological processes. In the chemical process ethanol is produced by ethylene hydration, while the microbiological route is produced by fermentation using yeast *Saccharomyces cerevisiae* yeast, mainly [8]. In the chemical process, ethanol is manufactured by reacting to ethene with steam. The formation of the ethanol is exothermic, and the reaction is reversible. In equation (1) is presented the chemical reaction

$$CH_2 = CH_{2(g)} + H_2O_{(g)} \leftrightarrow CH_3CH_2OH_{(g)} \Delta H = -45 KJ \cdot kmol^{-1} \tag{1}$$

Currently, the world ethanol production is carried out mainly by the biological pathway, referred to as alcoholic or ethanolic fermentation. During this process, sugars are converted into ethanol and CO_2 as secondary metabolites, cellular biomass, and energy. The feedstock employed is diverse, The United States of America produces ethanol from corn, Brazil bases its production process on sugar cane, the European Union from sugar beet, maize, wheat, barley, and rye. China is the fourth ethanol producer in the world, their production process is based on corn, wheat, rice, and sorghum. However, independent of the biomass, the fermentation process using hexose sugars (C_6) to produce ethanol is developed according to the equation (2).

$$C_6H_{12}O_6 + O_2 \rightarrow biomass\left(CH_{1.83}O_{0.56}N_{0.17}\right) + CO_2 + H_2O \tag{2}$$

The production of ethanol from sugar cane is one of the most important processes in South America, especially in Brazil, Colombia, and Ecuador. During this process, the sugar cane is submitted to juice extraction, with the aim to obtain a syrup rich in sugars, after which it must be sterilized to inoculate yeast, specifically *Saccharomyces cerevisiae*, which is perhaps one of the most studied and domesticated for industrial purposes.

Ethanol production using corn as feedstock requires more steps, mainly because the starch present in corn, is not metabolized directly by the yeast, therefore, is necessary to break down the starch into monomers of glucose, this is commonly carried

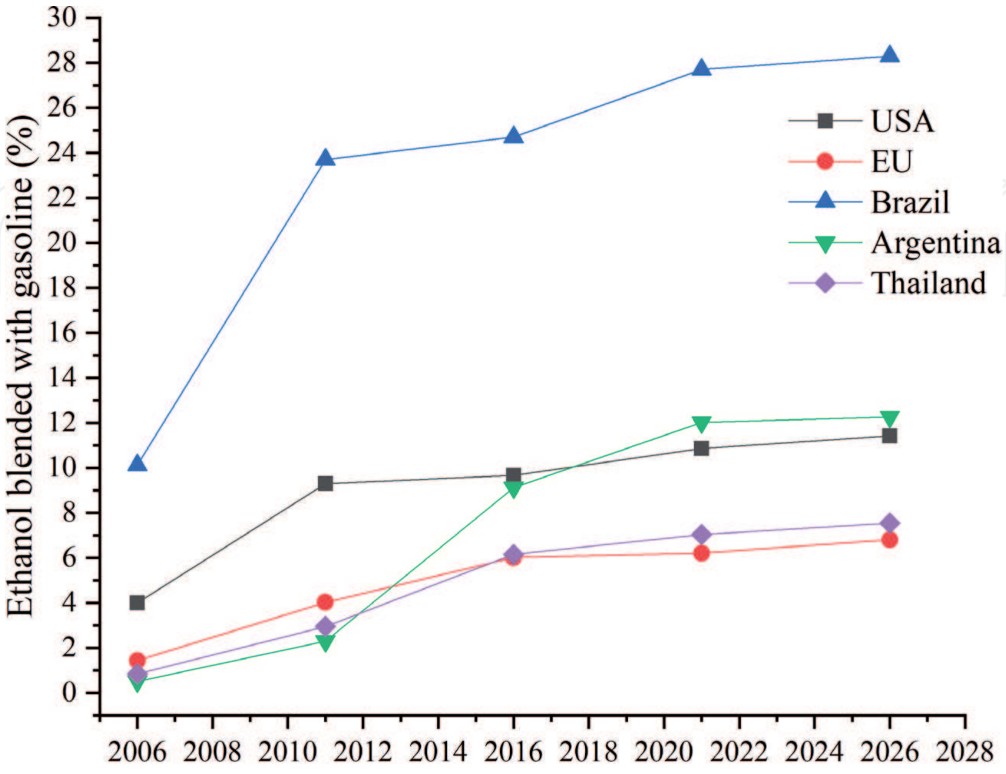

Figure 2.
Percentage of blended ethanol with gasoline in the largest producers of alcohol in the world.

out using enzymes such as alpha-amylase [9]. After monosaccharides solubilization, the fermentation process and downstream operation are like those carried out by sugarcane.

In all cases, it is mean indifferent of the feedstock used, the biomass must be pretreated with the aim to solubilize the sugar in the monomeric glucose form, for subsequent fermentation, from the fermentation broth, the water, nutrients, and salts contained in the mixture must be removed to obtain ethanol at the azeotropic point or hydrated ethanol. This operation is commonly developed by a sequence of distillation operation units.

From an economic point of view, the industry of ethanol is extremely attractive because it is used as a blending agent with gasoline and chemical building blocks. **Figure 2** shows the increased participation of ethanol in the blending with gasoline.

As is presented in **Figure 2**, the percentage of ethanol blended with gasoline has been increasing since 2006 in the main producers of alcohol in the world, except China. Brazil is the republic with the largest ratio of blending ethanol and gasoline near to 30%, regarding that in this country, the automotive industry manufactures cars with a flex engine, that is, the user can charge their vehicle with gasoline, alcohol, or a mixture of the two and the car will function normally.

Ethanol represents 90% of the total biofuels used, however, it is used as the chemical building block, different authors performed different studies about ethanol as a building block. From these studies are concluded that exist almost 12 final derivatives with high potential to be produced using ethanol as feedstock [10–12].

3. 2GE and 1GE ethanol controversy

The production of biofuels is particularly important for the reduction of the Global Warming effect and its direct consequence on climate change. However, ethanol production using different raw materials is subject to different analyses mainly by the food and fuel competition, added to different environmental, economic, and technical aspects. This section has presented an overview of the policies for ethanol production in the largest producers, their regulations, their financial aids, and production data.

First-generation ethanol (1GE) is the main liquid biofuel produced worldwide, with a global production of more than $25x10^3$ MGln. As was presented in **Figure 1**, the main producers are the United States of America and Brazil. In both countries, especially in Brazil, policies were launched and the government programs were created to promote the production and market of ethanol, mainly because of the energy crisis of the 1970s and the subsequent reduction of the dependence on imported fossil fuels.

In the United States of Amerca, 1GE is produced from corn, in this process, sugar must be produced from the starch present in corn, therefore more steps are involved during the ethanol manufacturing. To overcome this, the U.S. federal government, develop four main policies from 2002 to 2012, highlighting that alcohol production greatly expanded after the adoption of the U.S. Renewable Fuel Standard in 2005. The production increases 300 percent, passing from 4 Billion gallons in 2005 to 16 billion gallons in 2017, and is planned to reach 22 billion gallons in 2022 [13]. The policy developed by the government are listed below: (*i*) Subsidies on the feedstock used in the production of ethanol, mainly corn; *(ii)* A tax credit for blended ethanol. (*iii*) A mandate establishing a minimum volume of renewable fuel that must be blended with conventional fuels sold for transportation; (*iv*) Tariffs and other charges on imported ethanol [14].

In Brazil, two types of ethanol are used as fuel for transportation: hydrous and anhydrous alcohol. To support the ethanol industry, three main regulations were developed: (*i*) a mandatory blending of anhydrous ethanol in gasoline; *(ii*) a lower tax rate for hydrous ethanol than for gasoline; *(iii*) the Brazilian government's control over the price of gasoline another policy that has a major effect on the ethanol market. Probably the national program that includes all these policies is Proalcool Program, launched in 1974 with the aim to improve sugarcane harvesting, especially in the Sao Paulo State. One of the most important objectives of Proalcool was to guarantee fair competition and the equality of prices of alcohol with respect to sugar, paying for every 48 liters of anhydrous alcohol fuel the same value as that of a 60 kg bag of "standard" crystal sugar [15].

Then a summary of policies established in the United States and Brazil are presented in **Table 1**.

As is broadly summarized in **Table 1**, if the ethanol industry has not subsidies, the commercial price is difficult to be competitive against gasoline. This is one of the reasons because ethanol production currently generates controversy.

Moreover, 1GE production is the subject to study, mainly about the present and future competition between energy production and food consumption, which may lead to an increase in the prices of agricultural commodities, consequently causing famine in countries [16, 17]. Although this discussion is not new in the international agenda of bioenergy, this still highly controversial and generates a lot of discord. The issue of "turning food for the poor into fuel for the rich" [18].

Figure 3 shows the increase in the price of sugar and corn, in parallel with the production cost of ethanol in the United States and Brazil. Besides, according to the

Concept	U.S.	Brazil
Program Objective	**Reducing the nation's dependence on imported fossil fuels**	**Reducing the nation's dependence on imported fossil fuels**
Characteristics	1. Subsidies on feedstock used in the production of ethanol	1. A mandatory blending of anhydrous ethanol in gasoline
	2. Tax credit for blended ethanol	2. A lower tax rate for hydrous ethanol than for gasoline
	3. A law establishing a minimum percentage of Ethanol that must be blended with conventional fuels	3. Control over the price of gasoline
	4. Tariffs and other charges on imported ethanol.	
Value of the tax exemption/credit	US$0.54 per gallon (1990 to 20104)	R$0.28 per liter (2002-2007)
	US$0.51 per gallon (2005 to 2009)	R$0.18 per liter (2008)
	US$0.45 per gallon (2009 to 2011)	R$0.23 per liter (2009-2010)
		R$0.15 per liter (2011)
Charge of importation	US$0.54 per gallon of ethanol	R$0.0 for 187.5 million liters of imported ethanol
	2.5% of the import value	

Table 1.
Summary of the main policies in the two largest producers of ethanol.

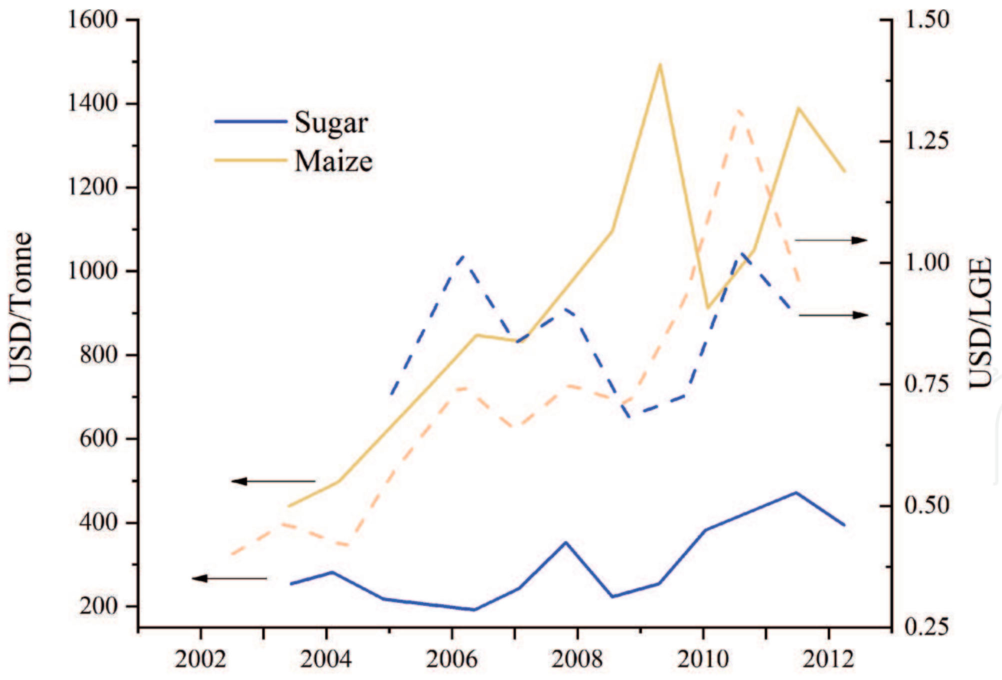

Figure 3.
Increase in the prices of corn and sugar according to the price of the gasoline equivalent (LGE).

data presented in **Figure 3**, it is well established that the price of sugar and corn has been increasing parallel to the increase in biofuels production.

To improve the environmental impact and avoid land and water competition between food and fuels, lignocellulosic material (LC) has been proposed as a viable alternative to produce liquid biofuels. LC is mainly composed of the three largest biomolecules, cellulose, hemicellulose, and lignin, their composition is a strong function of the type of biomass, harvesting time, final disposal of residues, and characterization method.

The most abundant residues are sugarcane bagasse (SCB), Oil Palm Empty Fruit Bunches (OPEFB), wheat straw, rice straw, corn straw, and soybean bagasse, are a great source of organic carbon, which would be converted to chemicals and biofuels. The LC is usually composed of cellulose, hemicellulose, and lignin. The plant matrix is organized in such a way that a microbial attack is avoided, allowing the transport of water and nutrients. This characteristic makes this type of biomass very recalcitrant, therefore, are necessary one or more steps to remove lignin, hemicelluloses to obtain fiber-rich cellulose, these steps are commonly called pretreatment of biomass, which can be chemical, thermochemical, or biological [19–21].

Currently, to improve the chain value of LC transformation is recommended the valorization of all fractions obtained during pretreatment, its mean, fractionated lignin in the form of black liquor, pentoses, mainly constituted by xylose and arabinose coming from hemicelluloses, and the glucose obtained by the enzymatic hydrolysis of cellulosic pulp. The lignin is commonly concentrated and used as an energy source to recover part of the energy expended in the process. Hemicelluloses traditionally, alternatives such as ethanol, xylitol, and furfural production were discarded. However, alternatives such as the production of ethanol, xylitol, for biological or chemical routes have been gaining attention from research centers and universities. The cellulose transformation to ethanol or some organic acids, such as citric, is probably the most extended and broadly studied and well established almost at a laboratory scale [22–24].

One of the bottlenecks of LC transformation into chemicals of high value-added and ethanol is the pretreatment, because from the economic point of view, at least 30% of the total capital investment (TCI), is required to build the pretreatment unit. From the technical view, homogeneous catalysis using acid and/or alkaline agents has proved to be the most suitable path, however, the generation of degradation products unidentified, then, commonly called humus, the formation of inhibitory compounds for biological transformation such as furfural, 5-HMF, acetic acid, mainly, and finally the low yields, almost 30% of the initial biomass is lost, makes this process a challenge for engineers and academics.

Several studies have been reported different strategies to optimize pretreatments, using steam explosion, sequential acid/alkaline, biological transformation, Ionic liquids, etc. However, in all cases, except for the biological one, biomass losses are considerable, the use of water and catalysts abundant, which makes these processes, from the environmental and economic point of view, subject to controversy [21, 25–33].

Added to the problems described below, in the case of ethanol production, two important aspects must be considered before developing a productive process. First, is the low yield obtained per kg of biomass treated, approximately by 1kg of biomass processed, are produced 100 g of ethanol would be produced. At this point is important to highlight other problem; the water present during the enzymatic saccharification and fermentation, makes the downstream process expensive and energy-intensive, therefore to develop a sustainable biorefining process, the ethanol production must be coupled with the production of high value-added molecules such as xylitol, furfural, organic acids, 5-HMF, and lignin valorization as reported by different authors [27, 34–37].

The discussion presented below had the intention of presenting the reader with an overview of the production of first and second-generation ethanol, its advantages, and associated problems, for the reader to generate their own conclusions.

4. Economic and environmental aspects of 2GE and 1GE

The 1GE production presents the two largest aspect subjects to controversy. First is the competition of land and water for crops intended for human consumption or fuel production. To overcome this problem, it has been suggested that ethanol production be carried out from lignocellulosic material from the processing of cereals, wood, oilseeds, and in general any type of biomass that is not suitable for human consumption. This section is discussed the general aspect of the economic and environmental impact of the production of both, 1GE and 2GE.

The 1GE production, especially in Brazil and the United States, has been focused on promoting rural development, with small farmers as the main beneficiaries. Based on the governmental policies and subsidies promoting ethanol production, the 1GE industry is well established and represents a market size estimated at USD 86.04 billion in 2020 (Before the sanitary emergency occasioned by SARS Covid-19). And is expected annual growth of 4.8% from 2020 to 2027 [10]. In a 1GE industry, moreover, than ethanol, exist the distilled grains, rich in carbohydrates, lipids, and protein, which can be used as byproduct to improve the economical profit [38].

On the other hand, it is 2GE, despite a promising alternative to reduce the greenhouse effect, this feedstock is not food competitive, currently is not a well-established industry with the largest production volume. Brazil is probably the country with the most advanced technology for the transformation of lignocellulosic material into bioethanol, using as feedstock the sugarcane bagasse and trash obtained from the processing of sugarcane for ethanol or refined sugar production [39].

The 2GE production using different feedstocks is broadly studied and numerous scientific reports are presented every year. From these reports, is clear that monumental efforts using various strategies have been envisioned to discover the best pretreatment method for converting biomass into fermentable sugars [40].

With the aim to develop a feasible process from the economic and energetic perspective, the two largest strategies have been reported. First is the combination of different pretreatment techniques, such as acid/alkaline pretreatment, steam explosion, CO2 explosion, ammonia fiber explosion, hydrogen peroxide treatment, Ionic liquids, ultrasonic, microwaves, and biological treatments have been studied, with two purposes mainly; first obtained the highest yields of sugar and second, the cost reduction. Parallel to these, the valorization of each fraction obtained during pretreatment, its mean, pentoses, lignin, and hexoses, for the production of molecules of high value-added, such as xylitol, furfural, 5-HMF, levulinic acid, succinic acid, fractionated lignin, to name few examples. The second strategy under study is the discovery (by isolation from nature or genetic manipulation) of robust strains that have excellent abilities to ferment hydrolyzed sugars with high yields and the largest tolerance to ethanol concentration. This strategy also seeks strains capable of fermenting pentoses for ethanol production with the objective of increasing the overall yield of alcohol production [41, 42].

From the economic evaluation of ethanol production reported in the literature [27, 43–46] is well established the following conclusions:

- The installation of a biorefinery process stand-alone using as feedstock lignocellulosic biomass is not feasible.

- The production of ethanol without valorization of the other fractions obtained during pretreatment stages is not recommended from the economic perspective.

- The Net Energy Value would be negative for the 2GE production, this means that more energy is used in the process than can be delivered through the sale of alcohol.

From the literature review and research did, we have established that the pretreatment unit is the most intensive process in economic and energetic terms, which makes the ethanol production from lignocellulosic biomass not feasible. However, the valorization of all fractions obtained during pretreatment, it would improve the economic profit and make the biorefinery process feasible from the economic point of view.

5. Future scenario for ethanol production

The development of new genetically modified strains will be one of the main advances in ethanol production. The traditional strains of *S. cerevisiae* used in the production of 1GE continue to be studied to increase yield, productivity, and tolerance to stress [47, 48]. New cultivation techniques are also being developed with the implementation of *S. cerevisiae* flocculant strains [49]. The use of these engineered strains allows the fermentation to continue because the microorganism has the capacity of auto-flocculation, settling at the bottom of the tank, and allowing higher productivity of ethanol.

The advanced strains of *S. cerevisiae* can metabolize mainly C6 sugars, such as glucose and fructose. However, from a 2GE perspective, lignocellulosic biomass can generate both C6, from the cellulosic fraction, as well as C5, as xylose and arabinose present in the hemicellulosic fraction. Thus, the use of lineages that do not have the capacity to synthesize C5 sugars with the same efficiency as C6 is a challenge to produce 2GE. Some yeast species are naturally capable of producing ethanol from xylose, such as *Candida shehatae*, *Pichia* (*Scheffersomyces*) *stipitis*, and *Pachysolen tannophilus* [50]. The use of two separate fermentation, one using cellulose hydrolysate and the other with hemicellulose hydrolysate may be the most viable alternative. Since C6 processing is already optimized with *S. cerevisiae*. Another problem with hydrolyzed broths is the presence of inhibiting compounds, such as acetic acid, furfural acid, and HMF, which can inhibit both the growth and viability of yeast and the metabolism of converting glucose to ethanol. Thus, strains resistant to inhibitory compounds are pivotal for the implementation of a biorefinery.

There is a great economic and environmental trend in the reuse of processing waste, such as lignocellulosic biomass. The productive chain of the sugar-alcohol industry can be considered the closest to a biorefinery concept. Since many wastes and by-products are no longer seen as disposable, but rather as new raw materials, impacting the price of sugar and ethanol. For example, in factories that use sugarcane, sugarcane bagasse is used to generate steam and energy by burning the residue, molasses, the by-product of the crystallization of raw sugar, in the generation of ethanol, and many investigations are carried out for the reuse of vinasse, a residue from the distillation of fermented juice, such as fertirrigation. Thus, a modern factory should contain, besides the production of sugar, the generation of bioenergy, biogas (biohydrogen and biomethane), biomolecules (organic acids, enzymes, and lipids), fertilizers, and microalgae [51].

6. Conclusions

The ethanol as biofuel is a reality, the 1GE production present a well stablished process and broadly used around the world, however, this may pose a threat to food safety. To overcome this problem, the production of ethanol using lignocellulosic material has been proposed, this appear as the most prominent alternative in terms of technological maturity. Nevertheless, the bottleneck is in the pretreatment stages, which are necessary to make fermentable sugars, therefore, standalone biorefinery process, using lignocellulosic biomass are not feasible for ethanol production. In this way, different techniques have been proposed to improve economic benefit, such as the production of value-added molecules or coupling 2GE to 1GE ethanol unit process. From the social, is well stablished that the incentives for harvesting different crops such as corn, sugarcane, wheat, rye, etc., are necessary to stimulate and benefit small producers, also, to obtain the ethanol price competitive with petroleum. Probably the environmental impact of 2GE is the most crucial, it is subject to criticism and analysis, because is not well stablished de real effect of their production, according with parameters such as CO2 liberation, water consumption, land deterioration.

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Conflict of interest

The authors declare that there is not conflict of interest

Author details

Jesús David Coral Medina[1,2]* and Antonio Irineudo Magalhaes Jr [2]

1 Department of Industrial Engineering, Cooperative University of Colombia, Campus Pasto, ESLINGA Research Group, 520002 Pasto, Nariño, Colombia

2 Department of Bioprocess Engineering and Biotechnology, Federal University of Paraná, P.O. Box 1911, 81531-990 Curitiba, Paraná, Brazil

*Address all correspondence to: jdcoralm@gmail.com

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