UNIVERSIDADE FEDERAL DO PARANÁ

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BRAZILIAN AGRO-INDUSTRIAL BY-PRODUCTS NEXUS AS A POTENTIAL IN MIXED BIOETHANOL SUSTAINABLE PRODUCTION

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Artigo apresentado como requisito parcial à conclusão do curso de Pós-Graduação MBA EM GESTÃO ESTRATÉGICA EM ENERGIAS RENOVÁVEIS E BIOCOMBUSTÍVEIS, Setor de CIENCIAS AGRARIAS, Universidade Federal do Paraná.

Orientador: Prof. M. Sc. Marcelo Langer

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Kim Kley Valladares-Diestra

RESUMO

O crescimento da população em todo o mundo está aumentando, esse crescimento leva a uma maior necessidade de energia para as diferentes atividades humanas. Os biocombustíveis surgem em resposta à necessidade de novas energias, tendo como principal característica a geração de menos emissões de gases com efeito estufa em comparação com os combustíveis fósseis, evidenciando ser mais eco amigáveis. Uma fonte interessante na produção de biocombustíveis é a biomassa lignocelulósica, com um grande potencial de produção em escala mundial. No Brasil, a produção de biomassa lignocelulósica é feita principalmente pelo setor agrícola, setor que tem um grande impacto na economia local e nacional, gerando diferentes subprodutos que podem gerar impactos negativos ao meio ambiente. Esses coprodutos têm um grande potencial na produção de biocombustíveis devido à sua composição rica em polissacarídeos, embora sua estrutura rígida e recalcitrante exija a necessidade do uso de pré-tratamentos. O pré-tratamento é uma das etapas mais importantes no processo de produção de bioetanol a partir da biomassa lignocelulósica, por isso existem diferentes métodos, como físicos, químicos e biológicos. Neste trabalho se fez um estudo sobre as diferentes literaturas publicada na produção de bioetanol, obtendo-se parâmetros de produção de primeira e segunda geração, com os quais se planejaram quatro cenários de produção de bioetanol. Seguidamente determinou-se um processo de uso eficiente da cana de açúcar no aumento de produção de bioetanol por médio de implantação de usinas mistas de primeira e segunda geração, aumentado de uma produção inicial de 10.2 L de bioetanol de primeira geração para 146.02 L de bioetanol por tonelada de cana de açúcar em uma produção mista (aumentando em mais de 50% a produtibilidade nos quatro cenários estudados). Ademais, foram aplicados conceitos de biorefineria na escolha dos melhores pré-tratamentos, para diminuir os impactos ambientais, diminuir a geração de gases de efeito estufa e adicionalmente obter novos materiais e produtos químicos de alto valor agregado que aumentem as ganancias econômicas das indústrias.

Palavras-chave: Bagaço de cana, biorefinarias, bioetanol, biomassa lignocelulósica, coprodutos agrossilvipastoris

ABSTRACT

Population growth worldwide is increasing, this growth leads to a greater need for energy in different human activities. Biofuels arise in response to the need for new energies, having as their main characteristic the generation of less greenhouse gas emissions compared to fossil fuels, showing that they are more eco-friendly. An interesting source in the production of biofuels is lignocellulosic biomass, with a great potential for production on a global scale. In Brazil, the production of lignocellulosic biomass is done mainly by the agricultural sector, a sector that has a great impact on the local and national economy, generating different by-products that can generate negative impacts on the environment. These co-products have great potential in the production of biofuels due to their composition rich in polysaccharides, although their rigid and recalcitrant structure forces the need to use pre-treatments. Pretreatment is one of the most important steps in the process of producing bioethanol from lignocellulosic biomass, so there are different methods, such as physical, chemical and biological treatment. In this work, a study was made on the different literature published in the production of bioethanol, obtaining first- and second-generation production parameters, with which four scenarios of bioethanol production were planned. Then, a process of efficient use of sugar cane was determined to increase bioethanol production by means of implantation of first- and second-generation mixed plants, increased from an initial production of 10.2 L in first generation to 146.02 L of bioethanol per ton of sugar cane in mixed production (increasing productivity by more than 50% in the four scenarios studied). In addition, biorefinery concepts were applied in the choice of the best pre-treatments, to reduce environmental impacts, decrease the generation of greenhouse gases and additionally obtain new materials and chemicals with high added value that increase the economic gains of industries.

Keywords: Sugarcane bagasse, biorefineries, bioethanol, lignocellulosic biomass, agrossilvipastoris by-products

SUMARY

INTRODUCTION

Population growth continues to increase, by the year 2030 the world population is expected to reach 8,500 million and 9,700 million in 2050. This growth leads to greater need and use of energy, it is estimated that total global energy consumption will grows considerably in 2040, projecting that world energy consumption will grow by 28% between 2015 and 2040 (ENERGY, 2019). Ethanol based on corn and sugarcane is a promising substitute for gasoline production, especially in the transport sector but may lead to the nexus and conflict of ‘‘food vs fuel” with the increase of world population (KABIR *et al.*, 2010).

Bioethanol obtained from lignocellulosic biomass, being an alternative source of renewable energy and be considerate a biofuel, could supply the growing energy market. However, there is an urgent need for research, development and fine tunings for an economically viable process in bioethanol production. Lignocellulosic biomass is a potential source in the production of different products, mainly second-generation bioethanol, because is produced in high quantities by agro industry and it does not compete with food production or animal feed. For other hand, due lignocellulosic biomass is very complex, some pretreatments are necessary to separate its main components as the cellulose, hemicellulose and lignin. In most cases, after enzymatic hydrolysis, the lignocellulosic biomass is converted in simple sugars such as glucose or xylose. For this reason, pretreatment is an important step in the production of bioethanol from lignocellulosic biomass (SINDHU; BINOD; PANDEY, 2016).

The wide variety of methods that exist for the pretreatment of lignocellulosic biomass can be classified into three basic categories: physical, chemical or biological. The physical methods are based on the increase of temperature, and pressure on the biomass reducing its recalcitrance; while chemical treatments are based on the use of reagents that generate interaction with the bonds of the different fractions of the biomass, causing a structure alteration of the lignocellulosic material. On the other hand, the biological treatments are based on the use of microorganisms, which in their development produce an enzymatic complex layers of disintegrating the lignocellulosic biomass each method or combination of them generate a different effectiveness for the type of lignocellulosic material, improving in the majority of cases the digestibility of biomass, increasing the yield of the desired products (JEDRZEJCZYK *et al.*, 2019)

The acceleration in research for a more efficient conversion of lignocellulosic biomass to energy, would generate greater competitiveness in production costs of biofuels such as bioethanol, thus offering an efficient output to the use of fossil fuels and supplying a great growth production for energy consumption. Lignocellulosic biomass is particularly suitable for energy applications due to its large-scale availability, low cost and that can be sustainable produced (BRODEUR *et al.*, 2011).

The general objective of the work is to show a sustainable process in the mixed production of bioethanol(first and second generation) with the use of sugar cane (main agro-industrial product in Brazil), also valuing the use of by-products such as sugarcane bagasse in order to propose the implementation of an economically viable lignocellulosic biorefinery

1 LIGNOCELLULOSE BIOREFINERIES

In recent years the bioeconomy has emerged as a sustainable development strategy, this is defined as the production of renewable resources, mostly of biological source, applied in the production of products with high added value (HASSAN; WILLIAMS; JAISWAL, 2019). Within this process, it is very important to highlight the management of by-products that are taken as new raw materials for the elaboration of other products, while avoiding the generation of waste. This strategy and its action plans increase and drives business volumes, so the bioeconomy also generates financial gains, for example in the European Union a profit of 2.09 billion euros was obtained in 2008 and reached 2.29 billion of euros in 2015 (PIOTROWSKI; CARUS; CARREZ, 2016).

Biorefineries represent a vital component within the future global economy and mainly within the bioeconomy, they also contribute greatly to decrease production of greenhouse gases, being more environmentally friendly, fostering and stimulating the use of circular bioeconomy based on use, reuse and recycling. Especially by efficient management of different by-products generated within the production processes, this cycle is also known as green economy.

A biorefinery is considered as an integrated production system that uses raw material such as biomass to produce a range of value-added products (HASSAN;

WILLIAMS; JAISWAL, 2019). Many different materials are used as raw material for a biorefinery, but lignocellulosic biomass stands out with a particular interest, due to its great abundance in the earth and its main characteristic of being renewable. Lignocellulosic biomass is very diverse and in biorefineries can be used residues derived from the forests and the agriculture.

Lignocellulosic biomass is very complex and relatively difficult to decompose, because sugars are trapped in their recalcitrant structure that requires multiplex pretreatment steps to release them (HASSAN; WILLIAMS; JAISWAL, 2018). The main components of lignocelluloses are the polymers of cellulose, hemicellulose and lignin that are responsible for creating the complex structure of cell walls in plants and also responsible for recalcitrance. Lignocellulose is also formed by different organic compounds of less presence such as proteins or inorganic matter such as water, silicates, sulfates, carbonates and nitrates (VASSILEV *et al.*, 2010, 2012). On the other hand, the proportion of the main components within lignocellulosic biomass will depend on the type of plant and parts of the plant used, for example, the cellulose content in wood is greater than in leaves or straw, while the leaves and straw contain more hemicellulose (BAJPAI, 2016).

In **Figure 1** can be observe the stages of development in a process of biofuel production from lignocellulosic biomass. Applying bioeconomy approache we can make the production cycle sustainable and renewable. Starting with agriculture where plants fix the CO_2 present in the atmosphere, transform it in plant biomass or reserve as energy. In next step food and timber industry uses this biomass to process raw materials generating new products; these industrial processes generate a high production of by-products with high lignocellulosic content, which can be used again as raw material in biofuels production. In the transformation of these by-products, rich in complex polysaccharides, pretreatments are used for decrease recalcitrance of biomass and generate fermentable sugars to be used in the fermentation of ethanol. These processes are carried out in specialized factories such as biorefineries, where all possible use is given to lignocellulosic material. Finally, the combustion of these biofuels generates energy and gases such as CO_2 which is released into the environment for then be fixed again into the plants generating a sustainable cycle of bioeconomic of use and production.

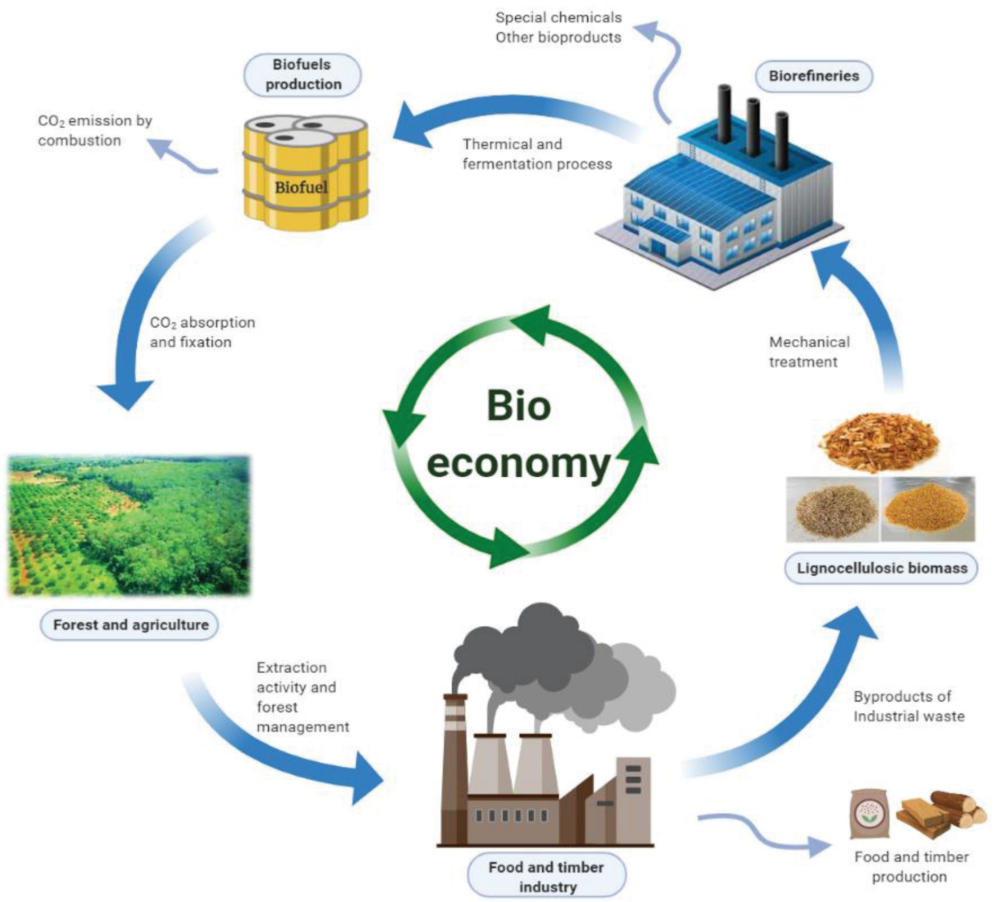

Figure 1 – Different steps of the bioeconomy.

Source: The author, 2020

2 AGROINDUSTRY BY-PRODUCTS PRODUCTION

In 2016, the area cultivated worldwide was 1,384.8 million hectares (FAOSTAT, 2017), producing millions of tons of cereals and other crops destined mainly to the food industry, this industry generates alarming environmental concerns because in the process of food production generates a large number of different by-products, which if not properly destined, can generate a negative environmental impact. These by-products mainly derivate from the plants considered as lignocellulosic biomass source and they could be used as alternatively input in bioethanol production generating a new potential source of energy production.

In Brazil, the agricultural industry is one of the most important sectors at an economic level, according to the FAO between the years 2015-2017 in Brazil, an approximate 76.4 million hectares were cultivated with an approximate production of 1,048.2 million tons of crops and derivate, producing 459.2 million tons of CO_2 equivalent emissions in 2017 (FAOSTAT, 2019). One of the factors that contributes to negative environmental impact is the high quantity and poor management of by-products that the agricultural industry produces.

The Brazilian's main agriculture products are sugarcane, soybeans, corn, cassava, oranges and rice. The **Figure 2** shows, that sugarcane is accounting for approximately 72% of all agricultural production, with an average production of 758.5 million of tons, soybeans and corn in turn had a production of 114.5 and 97.7 million tons respectively, which represents 9.7% and 7.8% of the total agricultural production in Brazil for 2017 (FAOSTAT, 2019). The main by-products obtained in the processing of these foods are sugarcane bagasse, soybean meal, corn stalk, cassava bran, orange peel and rice bran (**Table 1**). It is, also noted the vast majority of agro-industrial by-products have a content rich in polysaccharides, which demonstrates their high potential for bioethanol production, and on the other hand some by-products such as soybean has high protein content that can also be used in biorefineries.

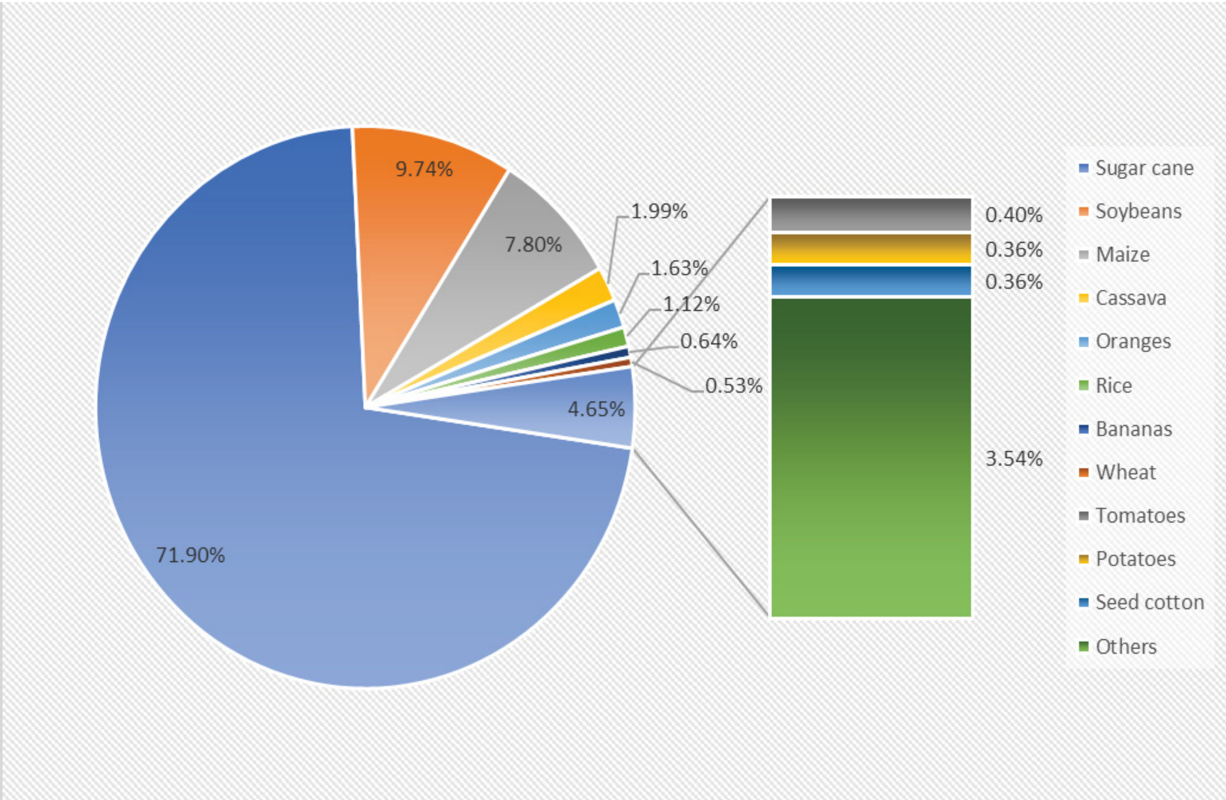

Figure 2 – Percentage of Brazilian crop production between 2015-2017
SOURCE: Food and Agriculture Organization of the United Nation (FAOSTAT, 2019)

The different agricultural by-products produced are directly related to the different regions of Brazil as well as to the agricultural practices and technologies used for cultivation, harvesting, transportation, storage and processing (CARRILLO-NIEVES *et al.*, 2019). As shown above, the main product produced in Brazil is sugarcane, generating approximately 245 tons of sugarcane bagasse annually, this by-product of the sugarcane and alcohol industry has a high content of polysaccharides, mainly of cellulose (**Table 1**), profiling as one of the main biomasses used in the production of second-generation alcohol.

Table 1. Principal products and agro-industrial wastes in Brazil

Product	Production in Brazil (million tons)	Main By-product	Percent estimate of by-product	By-product composition (%)	Current use of by-product	Reference
Sugarcane	759.1	Sugarcane Bagasse	30-34% of cane	45 % cellulose, 28% hemicellulose, 20 % lignin, 5% sugar, 1% mineral and 2% ash	Burn for electricity and used in animal feed	(NIKODINOVIC-RUNIC *et al.*, 2013; SANTOS *et al.*, 2016)
Soybean	102.8	Soybean meal	55-65% of grain	47-49 % protein, 3% crude fiber, 2-3% oil	Animal feed	(AGUIRRE TORIBIO; FONDEVILA LOBERA; GONZÁLEZ MATEOS, 2019; HEUZÉ; TRAN; KAUSHIK, 2017)
Cassava	21	Cassava “manipueira”[a]	30% in liquid	n/a	Biofuel/biofertilization	(FERREIRA; BOTELHO, 2001)
Orange	17.2	Orange peal	47.68% of fruit	Cellulose 13.61, Hemicellulose 6.10 and Lignin 2.10	Essential oil / pectin/ dietary fiber	(CARRILLO-NIEVES *et al.*, 2019)
Rice	11.7	Rice bran	5-10% of grain	15.5 % cellulose, 31.1% hemicellulose, 11.5 % lignin, 41.8 % other	n/a	(SUNPHORKA *et al.*, 2012)

[a] liquid produced after cassava flour extraction.

n/a: data not found

Source: The author, 2020.

Different researches report the high potential of Brazil in the production of second-generation alcohol with the use of cane bagasse, Walter et al. (2010) achieved an approximate production of 150 liters of alcohol per ton of bagasse. Mesa *et al*. (2011) shows that depending on the treatment conditions, alcohol can be obtained with varying amounts from 180-192 liters per ton of bagasse. Although the production of second-generation alcohol is promising, several studies show greater efficiency in the combined production of first- and second-generation alcohol, obtaining higher yields and lower production costs (BEZERRA; RAGAUSKAS, 2016).

3 BIOMASS PRETREATMENT FOR BIOFUEL

Pretreatment processes for lignocellulosic biomass are of paramount importance for the production of fermentable sugars or other chemicals with added value. This stage is indispensable in the processing of lignocellulosic biomass, because it causes a decrease in the recalcitrance of the material, making cellulose, lignin and hemicellulose more accessible and easily for hydrolyzed, by means of the use of enzymes or with the application of chemical products (JEDRZEJCZYK *et al.*, 2019). The extraction of the three rations of biomass is a bottleneck difficult to overcome by current methods, which generates a waste in the totally and integral use of these fractions to give products with greater added value.

The different pretreatment methods applied would facilitate additional processes in biomass, these pretreatments can mediate the efficient elimination of lignin, the degradation of hemicellulose, the reduction of crystallinity of cellulose and the increase of surface porosity (JEDRZEJCZYK *et al.*, 2019). These applied methods fulfill a key function for the following enzymatic hydrolysis steps in order to maximize the volumetric productivity of desired products capable of being fermentable.

The main expected effects, after pretreatment are: a) Production of easily digestible cellulose and hemicellulose by means of enzymatic hydrolyses; the improvement of the efficiency in the production of monosaccharides, avoiding the degradation of sugars produced during the process especially of pentose (xylose). b) Minimize the formation of inhibitors that could obstruct the fermentation processes. c) Recovery of the lignin fraction for the co-production of value-added compounds. d) Finally equipment, mainly reactors, with efficient heat transfer, minimizing energy use and increasing profitability of the process (BRODEUR *et al.*, 2011).

The most commonly used conventional methods are chemical, physical and biological, these methods seek to achieve a viable balance between the pretreatment efficiency, the cost and the environmental sustainability of the process, although this is usually difficult (HASSAN; WILLIAMS; JAISWAL, 2018). Physical pretreatment involves the decomposition of biomass size and crystallinity by grinding, improving mass transfer from the reduction in particle size (BRODEUR *et al.*, 2011). On the other hand, the biological pretreatment could be outlined as a promising and much more ecological method, avoiding the formation of inhibitors during the process, although in the current scenario there are some limitations in its application in pilot scale processes due to the incubation time for an effective delignification (SINDHU; BINOD; PANDEY, 2016).

3.1 HYDROTHERMAL PRETREATMENT

Hydrothermal pretreatment is a physicochemical method; it consists in the use of water at high temperatures, which generates a large amount of steam and high pressure within a closed system (reactor). Under these subcritical conditions, the hydrogen bonds of the molecules of water tend to dissociate forming acidic hydronium ions (H_30^+) and basic hydroxide ions (OH^-), due to this dissociation the subcritical water provides an acidic medium that generates the hydrolysis of polysaccharides, especially cellulose, producing fermentable monosaccharides sugars (KUMAR *et al.*, 2010). The lignocellulosic material when subjected to hydrothermal pretreatment processes generates the dissolution and degradation of hemicellulose; and the lignin is eliminated, facilitating accessibility to cellulose (AGBOR *et al.*, 2011).

The most important advantages of this pretreatment are: i. efficient elimination of lignin. ii. Solubilization of hemicellulose. iii. High yields in glucose production; minimal inhibitor formation for subsequent fermentations. iv. Low waste treatment costs, with few harmful effects on residual water. v. Do not present corrosive chemicals. vi. The avoiding the use of equipment with anticorrosive material. vii. and, reducing investment costs (BRODEUR *et al.*, 2011; GAUR *et al.*, 2017; YANG; TAO; WYMAN, 2018).

Unfortunately, the large water needs for this pretreatment dilute the amounts of monosaccharides sugars that can be obtained, losing sugars from hemicellulose, also dilute other value-added components and require a greater enzymatic load for enzymatic hydrolysis post processes (BHUTTO *et al.*, 2017).

3.2 CHEMICAL PRETREATMENT

Chemical treatments are used in order to modify the recalcitrant structures of lignocellulosic biomass. Within this pretreatment the most used methods are those based on acidic, basic solutions, use of ionic liquids, oxidizing agents or organosolv (JEDRZEJCZYK *et al.*, 2019). Depending on the chemical used and its concentration, different mechanisms of decomposition of lignocellulosic biomass may occur.

The appropriate choice of a chemical reagent for the treatment of biomass depends a lot on the objectives to be achieved, such as, for example, in obtaining the cellulose fraction, treatments with acid solutions are used, and in the case of a better hemicellulose recovery treatments are used with basic solutions.

3.2.1 Acid

Acid treatments involve the use of concentrated or diluted acids that act disorganized the rigid structure of the lignocellulosic material, mainly in the solubilization of hemicellulose, allowing that cellulose fraction be much more accessible to a subsequent enzymatic hydrolysate, in addition acid treatment hydrolyze the hemicellulose fraction and condense the lignin fraction. This treatment combined with high temperatures producing sugars, such as, glucose and mainly xylose from hemicellulose hydrolysis. The production of these sugars depends directly on exposure time of the biomass and treatment conditions (LLOYD; WYMAN, 2005). The most commonly used acid is dilute sulfuric acid (H_2SO_4) followed by hydrochloric acid (HCl), phosphoric acid (H_3PO_4) and nitric acid (HNO_3) (BRODEUR *et al.*, 2011).

Although chemical treatments have been the most used and studied in the hydrolysis of biomass, they have certain disadvantages that have not yet been overcome, such as the formation of fermentation inhibiting reagents like to furfural, hydroxymethylofurfural and acetic acid (mainly derived from hemicellulose) what would generate an additional process for its elimination (JÖNSSON; MARTÍN, 2016). The formation of a large amount of acidic waste, that needs to be treated, and neutralized to avoid further contamination of the environment; also, when using corrosive solutions in the process, the design of the reactors to be used must be robust and durable, increasing investment costs (BRODEUR *et al.*, 2011).

3.2.2 Basic

Alkaline treatments break down lignocellulosic biomass by attacking the intermolecular bonds of the polysaccharides, the alkaline agents act by saponifying the side chains of esters and glycosides resulting in their degradation. During the alkaline treatment the biomass increases the internal surface area generating swelling, depolymerization and de-crystallization of cellulose (CHENG *et al.*, 2010; HENDRIKS; ZEEMAN, 2009); partial solvation of hemicellulose and a structural alteration in lignin (IBRAHIM *et al.*, 2011). This treatment is more efficient in lignocellulosic material with low lignin contents and the most commonly alkaline reagents used are sodium hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide ($Ca(OH)_2$) and anhydrous ammonia (HENDRIKS; ZEEMAN, 2009; KUMAR *et al.*, 2009).

The main problems or disadvantages are long time process; presence of impurities, such as, alkaline ions of potassium, sodium, calcium and others that can affect the decomposition of organic biomass; in addition to the great difficulty of neutralizing highly alkaline residues produced after treatment (BHUTTO *et al.*, 2017; GIUDICIANNI *et al.*, 2018).

3.2.3 Green solvent

There is a growing interest in the use of ionic liquids (ILs) especially applied in the disintegration of lignocellulosic biomass, this interest has been increasing in recent decades due to the ability of these compounds to dissolve a wide variety of types of biomass. ILs are heterogeneous structures composed of an inorganic anion and an organic cation, have high polarity, thermal stability, low vapor pressure and exist as liquids at room temperature (BRODEUR *et al.*, 2011; JEDRZEJCZYK *et al.*, 2019).

The form of action of the ionic liquids within the biomass is by the formation of hydrogen bonds between the anion and the cellulose (forming hydroxyl protons) breaking the cellulose structure, generating more amorphous parts within the cellulose and increasing its accessibility for future enzymatic hydrolysis (BRODEUR *et al.*, 2011). In addition, according to the conditions of the treatment, ILs allow the dissolution of the hemicellulose and the lignin, allowing the recovery of the three biomass fractions (ZHANG; HU; LEE, 2017).

On the other hand, ILs break down cellulose chains without chemically modifying or degrading them, but if they reduce their degree of polymerization, they prevent the formation of fermentation inhibitors and by generating a low vapor pressure the ILs can be recovered by almost 99% in several operations, reducing process costs. Some ILs are biodegradable and do not cause toxicity like other chemicals (SUN *et al.*, 2011).

3.3 BIOLOGICAL TREATMENT.

Biological treatments are based in the use of microorganisms (fungus and bacteria) or in direct use of enzymes with high hydrolytic activity. Due to the hydrolysis power of enzymes, produced by microorganisms or placed directly, lignocellulosic biomass is degraded and decomposed. This method avoid use of chemical solvents and high reaction temperatures, for this reason are more environmentally friendly, generate less energy costs and produce less unwanted waste (SINDHU; BINOD; PANDEY, 2016; SINGH *et al.*, 2010).

In the biological treatment, the most commonly method used consists in the inoculation of microorganisms such as fungal and bacteria, which depending on their nature, degrade specific fractions of lignocellulosic biomass. White-rot fungi, brown-rot fungi, soft-rot fungi are widely used in these processes, causing changes in the structure and chemical composition of lignocellulosic biomass. Brown-rot fungi and soft-rot fungi mainly attack cellulose, but they can also generate minor impacts on lignin, while the white-rot fungi attacks the lignin fraction more efficiently, projected with better prospects for its use in the production of second generation biofuels in addition to being fungi with further study in this type of lignocellulosic biomass pretreatment (SUN; CHENG, 2002). On the other hand, the direct use of enzymes, due to its high specificity can generate a more targeted action. And according to the pretreatment objectives, lignin degradation for examples, can be used enzyme like lignin peroxidases, polyphenol oxidases, manganese-dependent peroxidases, and laccases ; but due to the high costs of enzyme production and that enzymes fail to penetrate lignocellulosic biomass efficiently this method is rarely used especially in the industry (CHEN *et al.*, 2010).

In the biological treatment process the decontamination of lignocellulosic material is necessary to eliminate possible competitive microorganisms, then the biomass is inoculated with the selected microorganism, only one type of microorganism can be used or in some cases a mist of microorganisms with synergistic activity in the deconstruction of biomass (SCOTT *et al.*, 1998). The incubation time may vary according to the type of biomass and microorganism used, as well as, due to the process conditions. It is of the utmost importance to maintain the optimal conditions for the growth of microorganisms and this can act in the biomass decomposition; among those conditions the most important are temperature, pH and humidity (SHARMA; XU; QIN, 2019).

Although, this methodology of pretreatment of lignocellulosic biomass causes a great interest, due mainly of being eco-friendly, and because there are important points that have not yet been resolved. As the complexity in the control of the process, the time and the speed of reaction are very high, when compared with other methods, generating an increase in processing costs, which is not interesting for large industries (CHEN *et al.*, 2010; SHARMA; XU; QIN, 2019).

4 CASE STUDY

The agricultural industry generates a large production of by-products, in the case of Brazil, sugarcane accounts for almost 72% of all agricultural production, due to the high demand for edible sugar, as well as, first-generation ethanol. This sugar and alcohol industry have several years of technical, and scientific development in Brazil, obtaining high efficiency values in first-generation ethanol production from sugarcane. However, production approaches based on a brown economy mean that different by-products are not used efficiently, and mishandling generates a negative impact on the environment. The high demand for alcohol in Brazil is also supported by public policies applied to energy and transport, making Brazil one of the few countries where ethyl alcohol is a fundamental part of the fuel industry (RICO; MERCEDES; SAUER, 2010).

This chapter shows the analysis of a better use of the alcohol production process, based on current techniques and with a bioeconomic approach to the use of biorefineries.

4.1 SUGARCANE BIOREFINERY SCENARIOS

The baseline scenario of ethanol production in Brazil represents the conventional system of first-generation alcohol production, based on the collection of sugarcane, extraction of juice and its fermentation to ethanol. On the other hand, the implementation of second-generation alcohol is still difficult, due to the high process and investment costs (CHANDEL *et al.*, 2019). Therefore, different researchers suggest the implementation of a mixed system in the production of bioethanol (first and second generation), where you can take advantage of the technology and equipment already used in the production of first-generation alcohol, reducing production costs and generating greater efficiency in the use of raw material (sugarcane).

For this study two types of first-generation alcohol production are proposed (with and without sugar production) and two types of pretreatment in second-generation alcohol production are used (hydrothermal pretreatment and chemical pretreatment) as shown in **Table 2**.

Table 2. Type of process in first and second bioethanol production

Type of production	Label	Description
First-generation	A	Ethanol production direct from sugarcane
	B	Sugar milling production + ethanol production from molasse
Second-generation	X	Ethanol production from bagasse using steam explosion
	Y	Ethanol production from bagasse using ionic liquid

Source: The author, 2020.

Based on the above, four different scenarios were studied in integrated first- and second-generation plant (**Table 3**).

Table 3. Scenarios raised for this study

Scenario	Integrated production	Description
I	A+X	Ethanol production direct from sugarcane + ethanol production from bagasse using steam explosion
II	A+Y	Ethanol production direct from sugarcane + ethanol production from bagasse using ionic liquid
III	B+X	Sugar milling production + ethanol production from molasse + ethanol production from bagasse using steam explosion
IV	B+Y	Sugar milling production + ethanol production from molasse + ethanol production from bagasse using ionic liquid

Source: The author, 2020.

4.2 PROCESS PARAMETERS, SUGARCANE AND LIGNOCELLULOSIC MATERIAL COMPOSITION

Data for the first- and second-generation ethanol production processes (**Table 4**) and sugarcane composition (**Table 5**) were obtained from different studies published in the literature, adapting according to the quantities of raw material used in this study. In cases where the data was not available, an estimate was used.

Table 4. Parameters used in the projection of bioethanol production

Parameter	Value	Unit	Reference
Sugarcane production	758,5	Mt	(FAOSTAT, 2019)
Area harvested	10,18	Mha	
Production yield	74,48	$ton.ha^{-1}$	
Industrial yield	85	$L_{ethanol}\ ton_{sugarcane}^{-1}$	(DE SOUZA DIAS *et al.*, 2015)
Distillation yield	99	%	
Ethanol conversion efficiency	0.208	$L_{ethanol}\ Kg_{molasses}^{-1}$	(SILALERTRUKSA; GHEEWALA; PONGPAT, 2015)
Sugar raw conversion efficiency	53	$Kg\ ton_{sugarcane}^{-1}$	
Sugar refined conversion efficiency	56	$Kg\ ton_{sugarcane}^{-1}$	
Molasse conversion efficiency	48.96	$Kg\ ton_{sugarcane}^{-1}$	
Steam explosion yield	59.72	$L_{ethanol}\ ton_{sugarcane}^{-1}$	(BITTENCOURT *et al.*, 2019)
Ionic liquid yield	47.62	$L_{ethanol}\ ton_{sugarcane}^{-1}$	(TURA; FONTANA; CAMASSOLA, 2018)

Source: The author, 2020.

Table 5. Raw material composition

Element	Content (% in weigh)	Reference
Sugarcane	100	(BARBOSA; HYTÖNEN; VAINIKKA, 2017; SANTOS *et al.*, 2016)
Sugarcane juice	35	
Sugarcane bagasse	32	
Sugarcane straw	33	
Sugarcane composition		
Sucrose	13.92	(BARBOSA; HYTÖNEN; VAINIKKA, 2017; DIAS, 2011)
Cellulose	5.95	
Hemicellulose	3.52	
Lignin	3.19	
Organic acid	0.56	
Salt and minerals	1.53	
Water	69.87	
Others	1.46	
Sugarcane juice composition		
Water	75	(DIAS, 2011)
Sucrose	21	
Reduction sugar	2.5	
Organic/inorganic not sugar	1.5	
Sugarcane bagasse/straw composition		
Cellulose (dry basis)	48.7	(BARBOSA; HYTÖNEN; VAINIKKA, 2017; BITTENCOURT *et al.*, 2019; TURA; FONTANA; CAMASSOLA, 2018)
Hemicellulose (dry basis)	23.2	
Lignin (dry basis)	23.1	
Extractives (dry basis)	1.1	
Ashes (dry basis)	3.9	

Source. The author, 2020.

4.3 RESULTS AND DISCUSSION

In **Figure 3,** it is possible to observe in detail the different steps of bioethanol production. It is starting from the raw material that is sugar cane we can separate this process into 3 large parts: the production of first generation ethanol (in green), the production of second generation ethanol (in blue) and the stages of the process where the first generation production as the second generation use the same equipment (pink).

4.3.1 First generation production

This process is the most used and developed in Brazil, with a productivity of reaches 85 liters of ethanol per ton of sugarcane (DE SOUZA DIAS *et al.*, 2015), as shown in **Figure 3.** The production is only directed for bioethanol (**Label A**), where the cane juice is extracted mechanically, followed by clarified of juice for removal of impurities by physicochemical treatments and concentrated by evaporating the water at 105°C. Finally, the juice concentrate rich in sugar is fermented by *S. cerevisae,* producing bioethanol and then purified by distillation. This process has a production yield of 67.05 grams of ethanol per kilogram of sugarcane.

On the other hand, the production of first-generation ethanol can also occur with the use of by-products from the extraction of edible sugar. Molasse is a by-product with a high concentration of sugars, which is used in the production of alcohol as seen in **Figure 3** (**Label B**), after obtaining this by-product follows the same processes for ethanol production as cane juice concentrated, producing 8.05 g of ethanol and 56 g of refined sugar per kilogram of sugarcane (SILALERTRUKSA; GHEEWALA; PONGPAT, 2015).

As saw, the first-generation alcohol production process can be relatively simple due to the great advance in technology already implemented, being able to obtain high yield of alcohol production, as well as the concomitant production of ethanol and sugar.

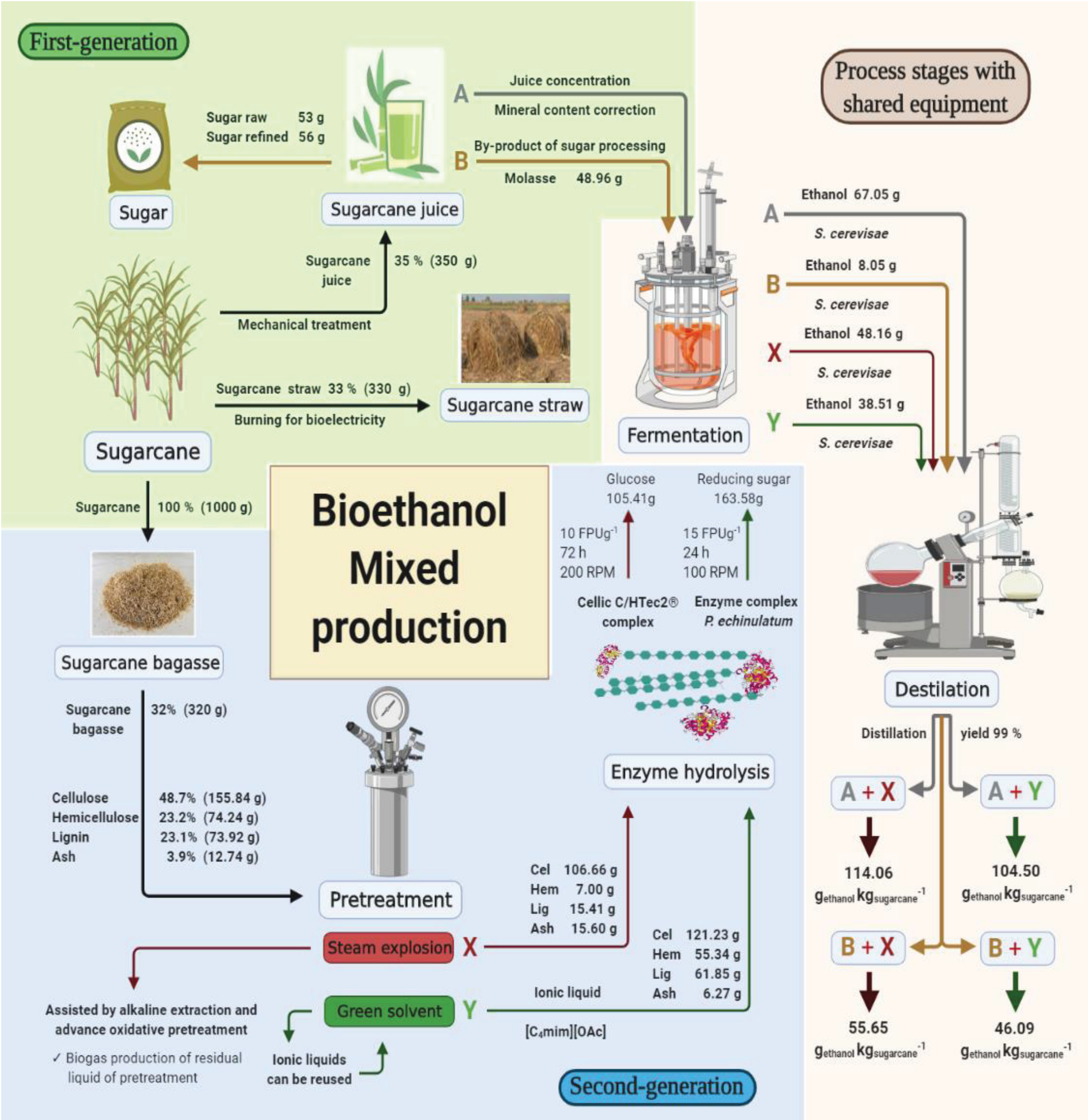

Figure 3 – Bioethanol mixed production designed in this study

Source: The author, 2020.

A (gray arrows): Ethanol production direct from sugarcane

B (brown arrows): Sugar milling production + ethanol production from molasse

X (icing arrows): Ethanol production from bagasse using steam explosion

Y (green arrows): Ethanol production from bagasse using ionic liquid

4.3.2 Second generation production

The second-generation alcohol production has been making great progress in recent years increasing ethanol production yields and decreasing process costs, making the final cost of ethanol produced more competitive. The sugarcane bagasse due to its composition (**Table 5**) is quite used in this type of process presenting a high efficiency in alcohol production.

The **Label X,** from **Figure 3,** shows the steam explosion process. This process assisted by a delignification of treated biomass, and finally exposed to an advanced oxidation treatment generates a solid biomass rich in cellulose. It is followed by hydrolysis with the enzymatic complex Cellic C/H Tec2 (Megazyme) generates an efficient production of fermentable sugars (especially glucose), which are fermented with *S. cerevisiae* obtaining a high efficiency in sugars bioconversion to bioethanol de 48.16 g of ethanol per Kg of sugarcane. It should be noted that in this process the liquid waste of each pretreatment can be used in the production of biogas (methanol) which generated an energy production that can be injected into bioethanol production process, reducing costs in energy expenditure (BITTENCOURT *et al*., 2019).

The second case raised (**Figure 3** - **Label Y**) shows the efficient use of ionic salt [C4mim] [OAc] as solvent in sugarcane bagasse pretreatment, presenting a good performance in biomass decomposition and high efficiency in enzymatic hydrolysis process. Hydrolysis was mediated by enzymatic complex produced by *P. echimulatum,* which have high performance in production of reducing sugars; these sugars were fermented by *S. cerevisiae* producing a value estimated of 38.51 g of ethanol per kg of sugarcane approximately. This process can present lower efficiency due to the possible fermentation inhibitors produced within the biomass pretreatment process, new types salts and tolerance microorganisms are being studying to prevent this happening. This treatment presents as one of its best advantages the reuse of the solvent in repetitive pretreatments (TURA; FONTANA; CAMASSOLA, 2018).

4.3.3 Integrated ethanol production

As previously stated, the idea of a mixed bioethanol production of first- and second-generation would lead to a better performance in use of sugarcane. Taking advantage of the fermentation and distillation processes already implemented in the first-generation bioethanol industry in second-generation process, significantly reducing investment costs.

In **Table 6**, the ethanol production results increase considerably when the second-generation ethanol is produced together. This increase is more significant especially in scenarios III and IV where first generation alcohol is not the main product and is produced from by-products (molasse).

Ethanol from second-generation production increasing the total yields of bioethanol production, prevents the accumulation of by-products and giving an efficient use this lignocellulosic biomass. Also this production process generate by-products rich in organic material and sugars (xyloses) can be used in energy production, through the biogas production, generating energy savings up to 65% (BITTENCOURT *et al.*, 2019)

Table 6. Ethanol and sugar integrated production from 1 ton of sugarcane

Scenario	Integrated production	Ethanol production (Kg)	First generation (L)	Second generation (L)	Ethanol production (L)	Sugar production (Kg)	Increase ethanol production (%)
I	A+X	114.06	84.98	61.04	146.02	0	71.83
II	A+Y	104.50	84.98	48.81	133.79	0	57.44
III	B+X	55.65	10.20	61.04	71.24	56	598.27
IV	B+Y	46.09	10.20	48.81	59.01	56	478.40

Source: The author, 2020.

It is also very important to highlight that diversification in the production of a company or industry helps to adapt to volatile markets, the price of alcohol is directly related to the price of fossil fuels, so a fall in the price of oil is negative in the demand of ethanol. That is why alcohol-sugar production companies can have more opportunities in volatile market, being able to modify their production from alcohol to sugar depending on the price and demand of each product; giving an advantage of adaptation to this type of industries.

Finally, different factors such as climate change due to global warming, energy security and social factors show a great interest in the development of second-generation alcohol. Generating the emergence of new companies or pilot-scale factories, such as, Raizen Energia and Gran Bio in Brazil, which together have a production capacity of almost 80 million liters of ethanol per year, using by-products of the sugarcane (CHANDEL *et al.*, 2019).

5 CONCLUSIONS

Brazil being an agricultural country has great potential in the production of by-products rich in lignocellulosic biomass, this biomass applied with the appropriate pretreatments can generate a large amount of fermentable sugars, which can be used in the production of bioethanol. To choose the use of a certain pretreatment and impacts that it can cause, and must be taken into account. The most appropriate being those that generate an almost zero impact on the environment, in addition, these pretreatments must be suitable for implantation in biorefineries.

Sugarcane is the most produced commodity in Brazil, so it generates interest in bioethanol production of first and second generation. The application of new techniques in obtaining second-generation bioethanol generates great development perspectives, although these processes are still expensive, the implementation of mixed production plants (first- and second-generation) could be the answer taking advantage of the use of different equipment and increasing efficiency in ethanol productivity.

The implementation of biorefineries would enhance the use of the raw material, generating a more efficient use of all the biomass and producing new materials or chemicals with high added value that can add to the financial gains within this industry (bioeconomy). These new processes applied in the production of bioethanol would generate a sustainable cycle of production and consumption of stove gases such as CO_2, helping to reduce global warming and other environmental impacts.

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