Chapter 2

Bioconversion of Hemicellulose from Sugarcane Biomass Into Sustainable Products

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Additional information is available at the end of the chapter

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1. Introduction

Sugarcane is main crop cultivated in countries like Brazil, India, China, etc. It plays a vital role in the economy of these countries in addition to providing employment opportunities [1]. Only in the 2012/13 Brazil harvest, for example, it was estimated that more than 602 million tons of sugarcane will be processed by the sugar-alcohol mills [2].

During the processing of sugarcane, the sugarcane straw (SS) is remained on field and do not presents suitable use. After the juice extraction from sugarcane stem, the fraction that is left over is called sugarcane bagasse (SB) [3]. Both residues (SB and SS) represent a sizeable fraction of agro-residues collected annually. The annual world production of sugarcane is ~1.6 billion tons, which yields approximately 279 million metric tons (MMT) of SB and SS [1, 4].

SB is used as a source of heat and electricity in sugar producing mills while SL is openly burnt on the fields causing environmental pollution. The harnessing of both residues via biotechnological routes into value-added products (xylitol, organic acid, industrial enzymes, ethanol, etc) is much more likely to be complimentary than competitive in the near term without jeopardizing the food requirements [5, 6, 7]. Both residues (SB and SS) are principally constituted of cellulose, hemicellulose and lignin. Among these constituents, hemicellulose is of particular interest because of its unique properties and composition. In the last two decades of research has been witnessed the technological development for the hemicellulose depolymerization into its monomeric constituents, mainly xylose, and their subsequent conversion into value-added products via microbial fermentation [8, 9, 10]. Dilute acid hydrolysis is a well established process for hemicellulose depolymerization, however, inhibitory compounds of microbial metabolism are also formed and should be reduced/eliminated prior to using the liquid in the fermentation process [8, 9]. On the other hand, enzymatic conversion of hemicellulose, that requires cocktail of enzymes for its breakdown, is slow, costly and requires combinatorial mixture of specialized enzymes [9]. The recovered sugar solution after hemicellulose hydrolysis contains primarily pentose sugars and the fermentation of these pentosans is problematic. Only limited numbers of microorganisms that use pentose are known and the fermentation of pentose sugars at industrial scale is not established yet [10, 11]. Generally, pentose utilizing microorganisms have slow growth rate, low osmotolerance and have poor resistance against inhibitors. The microorganisms that use pentose more extensively explored in laboratories are *Candida shehatae*, *Pichia stipitis*, *Pachysolen tannophilus* (for ethanol production), *C. utilis, C. intermedia*, *C. guilliermondii* (for xylitol production) and *Klebsiella oxytoca* ATCC 8724, *Bacillus subtilis*, *Aeromonas hydrophilia* (for 2, 3-butanediol production) [8, 9, 12].

Rather than summarizing all the literature on hemicellulose bioconversion from sugarcane agro-residues, we aim to highlight in this chapter technological developments focusing hemicellulose hydrolysis, detoxification of hydrolysates and microbial fermentation of sugars into sustainable products.

2. Sugarcane, bagasse and straw

2.1. Structure of sugarcane

The sugarcane basically consists of stem and straw. Stem is the part normally associated with sugarcane (cleaned cane). It is the piece of cane plant between plantation level and end node from last stem. The sugarcane stem are crushed to obtain cane juice, which is subsequently used for sugar (sucrose) or alcohol (ethanol) production. Sugarcane bagasse (SB) is the left over residue from stems after extraction of juice. It is normally burned to supply all the energy required in the process [13]. Sugarcane straw (or trash) (SS) is composed by fresh leaves, dry leaves and tops available before harvesting. Fresh (green and yellow) leaves and tops are the part of cane plant between the top end and the last stalk node. Dry leaves are normally in brownish color [14]. The SS is also normally burnt in the field after the harvest of the crop [15]. Potential applications of the leaves include: 1) as a fuel for direct combustion; 2) as a raw material for conversion by pyrolysis to char, oil and/or gas; and 3) as a raw material for conversion by gasification and synthesis to methanol. Potential applications of the tops include: 1) as a ruminant feed, either fresh or dried; 2) as a substrate for anaerobic fermentation to methane production; and 3) after reduction in water content, for the three energy uses listed for cane trash. Figure 1 presents the scanning electronic microscopy (SEM) of SS and SB before pretreatment. In the Figures 1A and 1B the SS was amplified 500 and 10.000x which reveal the presence of some vacuoles in the structure, which is not common in SB (Figure 1C).

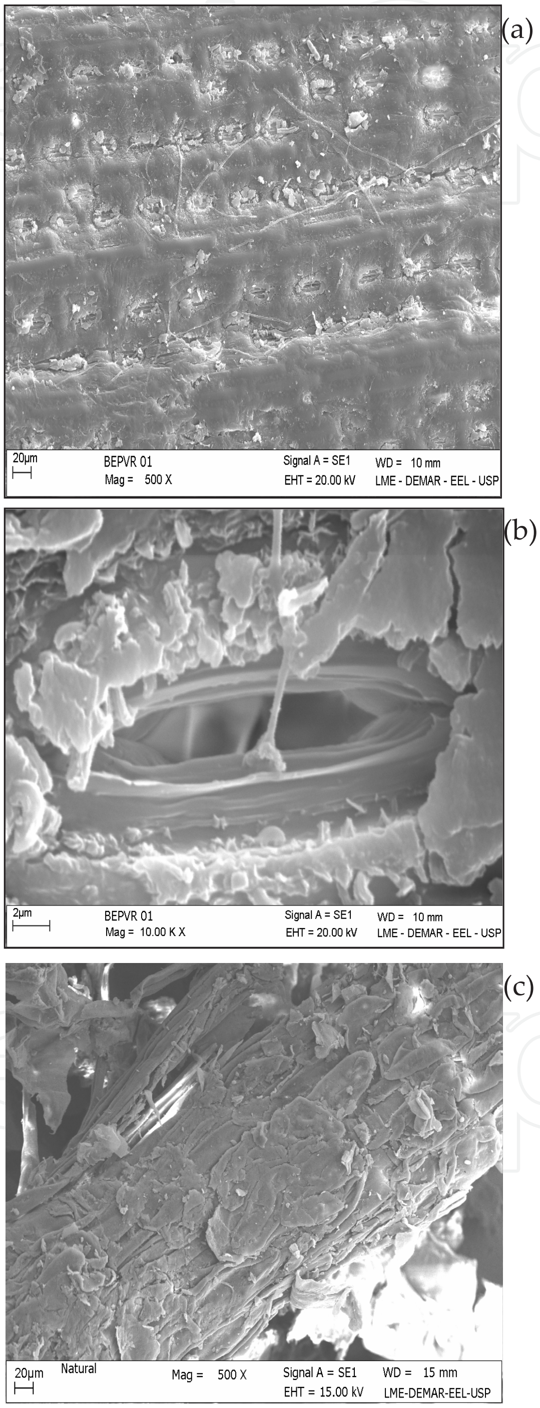

Figure 1. SEM of sugarcane straw (A) 500x and (B) 1000x [16] and sugarcane bagasse (C) 500x (Chandel et al., unpublished work).

2.2. Physical and chemical compositions of sugarcane

Physically, sugarcane is constituted by four fractions, whose relative magnitude depends on the agro industrial process: fiber, non-soluble solids, soluble solids and water. The fiber is composed of the whole organic solid fraction, non-soluble in water, originally found in the cane's stalk, and characterized by its marked heterogeneity from the morphological point of view. The non-soluble solids, or the fraction that cannot be dissolved in water, are constituted mainly by inorganic substances (rocks, soil and extraneous materials) and it is greatly influenced by the conditions of the agricultural cane processing and harvesting type. Soluble solids, fraction that can be dissolved in water, are composed basically of sucrose as well as other small chemical components such as waxes [17].

Bagasse and straw (trash), which are the focus of second generation ethanol production, are lignocellulosic materials chemically composed by cellulose, hemicelluloses and lignin. According to some works in the literature, sugarcane bagasse of the Brazilian territory is quantitatively composed by 38.8-45.5% cellulose, 22.7-27.0% hemicellulose and 19.1-32.4% lignin (Table 1). Non-structural components of biomass namely ashes (1.0-2.8%) and extractives (4.6-9.1%) are the other substances that are part of the chemical compositional of bagasse. The ash content of bagasse is lower than the others crop residues, like rice straw and wheat straw (with approximately 17.5 and 11.0% of this compound, respectively) and the bagasse is considered a rich solar energy reservoir due to its high yields and annual regeneration capacity (about 80 t/ha) in comparison with others agricultural residues, like wheat, grasses and tree (1, 2 and 20 t/ha, respectively) [3]. The bagasse also can be used as a raw material for cultivation of microorganisms for the production of value-added products such as xylitol and ethanol. Due to these and others advantages the bagasse is not only a sub-product of sugar industry, but it is a co-product with high added-value [3].

As can be seen in the Table 1, the chemical compositions of sugarcane bagasse samples varied widely. In fact, it is impossible to compare the composition of samples from different origins, performed by different laboratories and that do not use the same methods. Furthermore, factors like plant genetics, growth environment and processing conditions also influence the compositional analysis [18].

The large variation in the values of chemical components also is observed for the sugarcane straw, that it is composed approximately by 33.3-36.1% cellulose, 18.4-28.9% hemicellulose, 26.1-40.7% lignin (Table 2). Ashes (2.1-11.7%) and extractives (5.3-11.5%) are also present on the sugarcane straw composition.

When mechanically harvested, and depending on the harvesting technology applied, the range of straw that is collected and transported to the mill together with the stalks is 24% to 95% of the total trash available [19]. The amount of trash from sugarcane harvesting depends on several factors such as: harvesting system, topping, height, cane variety, age of crop (stage of cut), climate, soil and others. The average stalks yield per hectare was estimated to 83.23 tons/ha over an average of 5 seasons (cuts), resulting average availability of trash of 11.98 tons/ha (dry basis) [20].

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Component (%)	**Reference**						
	[22]1* Brazil	[23]2 Brazil	[24]3* Brazil	[25]4* Brazil	[26]5* India	[27]6 Cube	[28]7* USA
Cellulose	41.1	38.8	45.0	45.5	43.0	43.1	39.6
Hemicellulose	22.7	26.0	25.8	27.0	24.0	31.1	29.7
Lignin	31.4	32.4#	19.1	21.1	20.0	11.4	24.7
Ash	2.4	2.8	1.0	2.2	-	5.5	4.1
Extractives	6.8	-	9.1	4.6	-	-	14.3
Others	-	-	-	-	-	8.5	-

*Extractives-free basis; #Lignin and others

Extracting solvents: 1dichloromethane, ethanol: toluene (1:2), ethanol, hot water; 2none; 3water and ethanol; 4ethanol; 5none; 6none; 7not described

Table 1. Chemical composition (% w/w, dry basis) of Brazilian and worldwide sugarcane bagasse samples reported in the literature

Component (%)	**Reference**					
	[16]1* Brazil	[22]2* Brazil	[29]3* Brazil	[23]4 Brazil	[30]5 Brazil	[15]6 India
Cellulose	36.1	34.4	36.1	33.6	33.3	45.0
Hemicellulose	28.3	18.4	26.9	28.9	27.4	25.0
Lignin	26.2	40.7	26.2	31.8#	26.1	18.0
Ash	2.1	11.7	2.1	5.7	2.6	-
Extractives	5.3	11.5	5.3	-	-	-
Others	-	-	-	-	10.6	-

*Extractives-free basis; #Lignin and others

Extracting solvents: 1ethanol; 2dichloromethane, ethanol: toluene (1:2), ethanol, hot water; 3water; 4none; 5none; 6none

Table 2. Chemical composition (% w/w, dry basis) of Brazilian and Indian sugarcane straw samples reported in the literature

From the technological viewpoint, sugars that are present in the cellulosic (glucose) and hemicellulosic (xylose, arabinose, glucose, mannose and galactose) fractions representing the substrates that can be used in fermentative process for production of some sustainable products such as xylitol, butanediol, single cell protein, ethanol and xylitol. However, the close association between the three major fractions (cellulose, hemicellulose and lignin) of the lignocelulosic materials, like bagasse and straw, causes difficulties for the recovery of these substrates in the form of monomers with high purity. Therefore, to use these three constituents it is required a selective separation of each fraction by pretreatment techniques, delignification and hydrolysis, involving the breakdown of hemicellulose-lignin-cellulose complex [21].

3. Methods of separation of hemicellulose from cellulignin complex

The lignocellulosic materials are renewable resources which can be used to obtain sustainable products as well as value-added biomolecules [31]. However, cellulose, hemicellulose and lignin are arranged to form a highly recalcitrant structure [32], hindering the availability of carbohydrates for fermentation processes, representing a high barrier for the bioconversion of lignocellulosic materials [33]. Through a pretreatment process, the biomass components can be separated, releasing fermentable sugars such as xylose, arabinose and glucose and making the cellulose more accessible to the action of cellulolytic enzymes [34, 35]. This step is one of the most expensive step of biomass processing, thus, studies to lower the cost are extremely important [35].

According to Brodeur et al. [36], the typical characteristics that must be attained in a pretreatment process are: production of highly digestible solids that enhances sugar yields during enzyme hydrolysis; avoid the degradation of sugars; minimize the formation of inhibitors; recover the lignin for conversion into valuable co-products. Pretreatment process should be cost effective and environment friendly. All these features are considered in order that pretreatment results balance against their impact cost on downstream processing steps and the trade-off with operational cost, capital cost and biomass cost [37]. The pretreatments methods can be divided into physical, chemical, physic-chemical and biological [38]. Some methods of pretreatments as well as their advantages and disadvantages are shown in the Table 3.

Different types of biomass (woody plants, grasses, agricultural crops, etc) has different contents and proportions of cellulose, hemicellulose and lignin which determine the digestibility of the biomass [37]. There is not a universal pretreatment process for all biomass. Depending on the process and conditions used, hemicellulose sugars may be degraded to weak acids, furan derivates and phenolics that inhibit the fermentation process, leading to lower yields and productivities of the desired product [8]. Thus, the method of pretreatment used will depend on the type of raw material used, the objective of the process (the constituent to be degraded) and the product to be obtained, which will directly affect the cost benefit.

	Process	***Advantages***	***Disadvantages***	***Solubilized Fraction***			***References***
				Hemicel.	***Cel.***	***Lignin***	
Physical Pretreatments							
Milling	ball milling provides the reduction of particles size and breaks down the structure of lignocellulosic materials	- environment friendly - chemical addition is not required - inhibitors are not produced	- high power - high energy costs	Alteration in structure			[23] [39]
Pyrolysis	treatment with temperatures higher than 300ºC	- fast degradation of cellulose into H_2, CO and residual char	- high temperature - ash production		X		[40]
Physic-Chemical Pretreatments							
Steam Explosion or hydrothermal	structure compounds breakdown by heat addition in form of steam and forces by the moisture expansion	- needs few or no chemical addition - environment friendly	- inhibitors production	X			[41] [42]
Ammonia Fiber Explosion (AFEX)	expose the lignocellulosic material with ammonia to high temperature and pressure followed by a fast pressure release	- inhibitors are not produced - simple process -short time process	- cost of ammonia - ammonia recovery - depending of lignin content			X	[38] [40]
CO_2 Explosion	formation of carbonic acid and increase the hydrolysis rate of substrates	- more cost effective - inhibitors are not produced	- hard operation method		X	X	[40] [43]
Chemical Pretreatments							
Acid Pretreatment	dilute-acid hydrolysis of the lignocellulosic material	- low and medium temperatures	- equipment corrosion - inhibitors production	X	X		[10] [24] [35]
Alkaline Pretreatment	delignification process employing bases such as sodium hydroxide, calcium hydroxide (lime), etc	- low temperature - low pressure	- long processing time - environment pollution			X	[40] [44]

	Process	Advantages	Disadvantages	Solubilized Fraction			References
				Hemicel.	Cel.	Lignin	
Ozonolysis	the ozone incorporates conjugated double bonds and functional groups with high electron densities	- removal of lignin - inhibitors are not produced - ambient temperature and pressure	- large amount of ozone is required - expensive process	X		X	[45] [46]
Organosolv	simultaneous process of hydrolyses and delignification catalyzed by solvents and diluted acid solution	- facilitates the enzyme access - needs few chemical addition - low waste generation	- expensive process			X	[47] [48]
Wet Oxidation	occurs in the presence of oxygen or catalyzed air, sodium carbonate is the preferred catalyst	- released sugars without generation of inhibitors	- expensive process - high pressure	X		X	[9]
Biological Pretreatments							
Microorganism	modification of the chemical composition and/or structure of lignocellulosic materials employing microorganisms	- environment friendly	- low efficiency - considerable loss of carbohydrates - long processing time			X	[15] [38] [44]

Hemicel.: hemicellulosic fraction; Cel.: cellulosic fraction; X: solubilized fraction by the pretreatment

Table 3. Advantages and disadvantages of different methods of pretreatment

4. Hemicellulosic fraction

4.1. Structure of hemicellulose

Hemicellulose differs substantially from cellulose to be amorphous, which makes it more easily hydrolyzed than cellulose [49]. The hemicellulosic fraction reaches 40% of lignocellulosic material and acts as substance of reserve and support. This fraction presents branched structure composed by pentoses (D-xylose and L-arabinose), hexoses (D-galactose, D-mannose and D-glucose) and small amounts of acetic and uronic (D-glucuronic, D-4-O-methyl-glucuronic and D-galacturonic acids) acids [8, 21]. Other sugars such as L-rhamnose and Lfucose may also be present in small amounts. Xylose is the main carbohydrate present in the hemicellulosic fraction, representing about 80% of total sugars [35, 50].

The heterogeneous structure of hemicellulose with a low polymerization degree makes it interesting fraction for fermentation process. The open three-dimensional conformation of hemicellulose favors the diffusion of the catalyst in the molecule, providing a better yield of hydrolysis in mild conditions [51, 52].

The hemicellulosic fraction can be removed of lignocellulosic materials by some type of pretreatments, summarized in the Table 3, liberating sugars, mainly xylose, that subsequently can be fermented to sustainable products such as xylitol, butanediol, single cell protein and ethanol [24, 27].

4.2. Methods of detoxification of hemicellulosic hydrolysates

When the lignocellulosic matrix is breakdown by different types of pretreatments, particularly by dilute acid process, undesired compounds that are toxic for microbial metabolism are liberated and/or formed in addition of sugars. These products can be divided into three groups according to their origin: derived from sugars (furfural and 5-hydroxymethylfurfural), lignin derivatives (phenolics i.e. vanillin, *p*-hydroxybenzaldehyde, lignans, etc.) and weak acids (acetic, formic and levulinic) [53]. Several studies have shown that these byproducts generated during the hydrolysis of the hemicellulose fraction from different materials affect negatively the microbial metabolism, hindering the conversion of sugars in some products of interest [53, 54, 55].

Several chemical, physical and biological methods have been used for removing these byproducts present in the hemicellulosic hydrolysates. Some detoxification methods as well as their advantages and disadvantages are summarized in the Table 4.

4.3. Products from hemicellulose

Hemicelluloses have a wide variety of applications. They can be hydrolyzed into hexoses (glucose, galactose, and mannose) and pentoses (xylose and arabinose), can be transformed into fuel ethanol and other value-added products such as 5-hydroxymethylfurfural (HMF), xylitol, ethanol, butanediol, butanol, etc. In addition, hemicelluloses also can be converted into various biopolymers, like polyhydroxyalkanoates (PHA) and polylactates (PLA).

In industrial applications, hemicelluloses are used to control water and the rheology of aqueous phases. Thus, they may be used as food additives, thickeners, emulsifiers, gelling agents, adhesives and adsorbents [71]. According to Peng et al. [72], hemicelluloses have also been investigated for their possible medical uses such as ulcer protective [73], antitussive [74], immunostimulatory [75] and antitumor properties [76]. For example, xylooligosaccharides have been shown to have economic utilization in the pharmaceutical industry for applications such as treating viral and cancer processes in the human body [77, 78].

	Process	Advantages	Disadvantages	References
		Physical Methods		
Evaporation/ Concentration	removes toxic compounds by evaporation in a vacuum concentrator based on the volatility	- reduces volatile compounds as acetic acid, furfural, and vanillin	- increasing the nonvolatile toxic compounds as extractives	[56] [57]
Membrane	membranes have surface functional groups attached to their internal pores, which may eliminate metabolic inhibitors	- avoids the need to disperse one phase and minimize the entrainment of small amounts of organic phase	- high cost - selective removal of inhibitors	[58] [59]
		Physic-Chemical Methods		
Ion Exchange Resin	resins change undesirable ions of the liquid phase to be purified by saturating of functional groups of resins	- can be regenerated and reused - remove lignin-derived inhibitors, acetic acid and furfural - does not cause high sugars loss	- high pressure - long processing time - possible degradation of fragile biological product molecules - difficult to scale-up	[59] [60] [61] [62]
Overlimming	increase of the pH followed by reduction	- precipitate toxic compounds	- high sugars loss - filtration complexity	[63]
Activated Charcoal	adsorption of toxic compounds by charcoal which is activated to increase the contact surface	- low cost - remove phenolics and furans - minimizes loss of sugars	- filtration complexity	[60] [64] [65]
Extraction with Organic Solvents	mix of liquid phase to be purified and a organic solvent. The liquid phase is recovered by separation of two phases (organic and aqueous)	- recycling of solvents for consequent cycles - remove acetic acid, furfural, vanillin, 4-hydroxybenzoic acid and low molecular weight phenolics	- high cost - long processing time	[66] [67]
Vegetable Polymer	biopolymers are composed by tannins with astringent properties that flocculate inhibitors compounds	- low cost - biodegradable - minimizes loss of sugars - reducing toxic compounds	- cell death when the tannin content is high - significant volume loss	[68]
		Biological Methods		
Microorganism	specific enzymes or microorganisms that act on the inhibitors compounds present in hydrolysates and change their composition	- low waste generation - environmental friendly - less energy requirements	- long processing time	[56] [59] [69] [70]

Table 4. Advantages and disadvantages of different detoxification methods of hemicellulosic hydrolysate

Arabinoxylans are used as emulsifiers, thickeners, or stabilizers in the food, cosmetic, or pharmaceutical industries. Glucomannans are used in the food industry (as caviar substituent), whereas arabinogalactans have applications in the mining (for processing of iron and copper ores) or pharmaceutical industry (as a tablet binder or emulsifier). 4-O-methylglucuronoxylan is a water absorption agent and also presents antitumor activity [71].

4.3.1. Xylose and glucose

The D-xylose ($C_5H_{10}O_5$) is the main carbohydrate found in the hemicellulose fraction of sugarcane bagasse and straw. It is used as a sweetener for diabetics [79], as non-cariogenic sweetener [80], to enhance the flavor of food made from beef and poultry [81], to prepare marinades and baked [81] and as substrate in fermentation processes to produce different products, such as penicillin, biodegradable polymers and xylitol [50, 82]. Monomeric xylose from hemicellulose has a selling price of ~$1.2/kg [83]. It is known that in industrial scale, xylose is obtained from lignocellulosic materials rich in xylan. These materials are hydrolyzed in the presence of dilute acids. Then, the hemicellulose hydrolysates are purified, in order to remove the byproducts generated during the hydrolysis of hemicellulose. After the purification steps, xylose is recovered of purified media by crystallization [84].

D-glucose is also found in the hemicellulose fraction of sugarcane bagasse and straw and can be obtained by hydrolysis of cellulosic materials. Some compounds that are obtained from glucose fermentation are alcohols (ethanol, isopropanol, butanol, 2,3-butanediol, glycerol), carboxylic acids (acetic acid, propanoic acid, lactic acid, gluconic acid, malic acid, citric acid) and other products such as acetone, amino acids, antibiotics, enzymes and hormones [85].

4.3.2. 5-Hydroxymethylfurfural and levulinic acid

5-Hydroxymethylfurfural (HMF) ($C_5H_4O_2$), which is derived from the hexoses (6-carbon sugars) present in the hemicellulose, is produced by steam treatment followed by dehydration [85, 86, 87]. HMF is an intermediate in the production of levulinic acid from 6-carbon sugars in the biofinery process. HMF is very useful not only as intermediate for the production of the biofuel, dimethylfuran (DMF) and other molecules, but also for important molecules such as levulinic acid, 2,5-furandicarboxylic acid (FDA), 2,5-diformylfuran (DFF), dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid [88]. Glucose is still utilized in industry for the preparation of HMF because of its price lower than fructose [89].

Levulinic acid (4-oxopentanoic acid) ($C_5H_8O_3$) is a valuable platform chemical due to its specific properties. It has two highly reactive functional groups that allow a great number of synthetic transformations. Levulinic acid can react as both a carboxylic acid and a ketone. The carbon atom of the carbonyl group is usually more susceptible to nucleophilic attack than that of the carboxyl group. Due to the spatial relationship of the carboxylic and ketone groups, many of the reactions proceed, with cyclisation, to form heterocyclic type molecules (for example methyltetrahydrofuran). Levulinic acid is readily soluble in water, alcohols, esters, ketones and ethers. The worldwide market has estimated the price of $ 5/kg for pure levulinic acid [86].

4.3.3. Furfural and formic acid

Furfural (2-furaldehyde) and its derivatives, furfuryl alcohol, furan resins, and tetrahydrofuran, are produced in many countries from corn cobs, wheat and oat hulls, and many other biomass materials [90]. Furfural, which is derived from the pentoses (five-carbon sugars) present in hemicellulose, is produced by steam treatment followed by dehydration with hydrochloric or sulfuric acid [87, 90]. The market price of furfural was approximately \$1/kg compared with prices in 1990 of \$1.74/kg for furfural and \$1.76/kg for furfuryl alcohol [83, 86]. The most important furfuryl alcohol is used to produce furan resins for foundry sand binders. Tetrahydrofuran is made by the decarbonylation of furfural with zinc-chromium-molybdenum catalyst followed by hydrogenation. It is also made by the dehydration of 1,4-butanediol [87]. Other uses for furfural, such as production of adiponitrile, might be found if furfural prices were reduced by expanded production [90].

Formic acid (methanoic acid) is an important organic chemical which is widely used in industries. Recently, it received renewed attraction to be used as environmentally benign storage and transportation medium for hydrogen, the clean energy in future. Extensive studies have shown that hydrogen and CO_2 could be quickly and efficiently generated by the decomposition of formic acid by hydrothermal reaction or catalyst reaction. Also, some researchers have demonstrated that formic acid has the potential to direct power fuel cells for electricity generation and automobiles [91]. It is used extensively as a decalcifier, as an acidulating agent in textile dyeing and finishing, and in leather tanning. It is also used in the preparation of organic esters and in the manufacture of drugs, dyes, insecticides, and refrigerants. Formic acid can also be converted to calcium magnesium formate which can be used as a road salt. The current market price of formic acid is \$0.16/liter [86].

4.3.4. Xylitol

Xylitol is a polyol of five carbons ($C_5H_{12}O_5$) easily found in nature in many fruits and plants. Among them, the yellow plum is the vegetable that contains highest level of xylitol [92]. This polyol is an intermediate metabolite in the carbohydrate metabolism in mammals, with an endogenous production followed by assimilation of 5-15g per day in a normal adult. Xylitol is widely used as a sweetener by diabetics due to its slow adsorption and entrance in pathways which is independent of the insulin and does not contribute in rapid change of blood glucose levels [93].

This polyol, with anti-cariogenic properties, is employed in foods, dental applications, medicines and surfactants [94, 95]. In the dental applications, the use of xylitol reduces the salivary flow, reduce gingivitis, stomatitis and lesions to poorly fitted dentures. If used in toothpaste, its action enhances the action of sodium fluoride and chlorhexidine, increasing the concentrations of xylitol 5-P [96]. For human diet, the Food and Drug Administration classifies this product as “GRAS” - “Generally Recognized as Safe” [97].

At large scale, xylitol is produced by chemical reduction of xylose derived mainly of wood hydrolysates. This process consists in steps of acid hydrolysis of the vegetal material, hydrolysate purifications and crystallization of xylitol [92]. However, there are disadvantages in the chemical production such as the use of high temperature and pressure in the process and the purification steps with low efficiency and productivity [52]. In this context, the biotechnological production of xylitol from hemicellulosic hydrolysates is a promising process with great economic interest. This process can add value to the lignocellulosic residues, like sugarcane bagasse and straw, promoting a complete utilization of these materials, using the cellulosic and hemicellulosic fractions to obtain xylitol and others value-added bioproducts [98]. Among the microorganisms that produce xylitol, yeast, particularly the genus *Candida, Pichia, Debaryomyces* are the most employed due to their ability to convert xylose to xylitol, with significant yields [99]. Xylitol can be produced through microbial transformation reactions by yeast from D-xylose, or by both yeast and bacteria from D-glucose [100]. D-xylose can also be directly converted into xylitol by NADPH-dependent xylose reductase [101].

Considering xylose fermentation by yeasts, the main factors that should be controlled are: substrate concentration, cellular concentration, the presence of inhibitors, aeration flow, adaptation of the microorganism to the hydrolysate, temperature and pH [102, 103]. It can be found many works in the literature where these factors were studied extensively using the hemicellulosic hydrolysates obtained from different lignocellulosic materials. From sugarcane bagasse hemicellulosic hydrolysate, for example, Carvalho et al. [61] reported the production of 19.2 g/L of xylitol by *Candida guilliermondii*; Santos et al. [104] achieved 18 g/L of xylitol with a bioconversion yield of 0.44 g/g employing a fluidized bed reactor operated in semi-continuous mode with the same yeast; and recently, Prakash et al. [105] produced xylitol, with a yield and volumetric productivity of 0.69 g/g and 0.28 g/L.h, respectively, using *Debaryomyces hansenii*.

The world xylitol production exceeds 10,000 tons per year and is directed mainly to the food, pharmaceutical and cosmetics [106]. The American xylitol market is estimated at $159 million for 2012 while it expected $400 million to $500 million for global market [107]. From the Figure 2, it can be seen the average annual prices of xylitol from 1995 to 2007. Xylitol price has decreased over last decades until 2007 (Figure 2), however since 2009, the price of xylitol has increased to $4-5/kg [108].

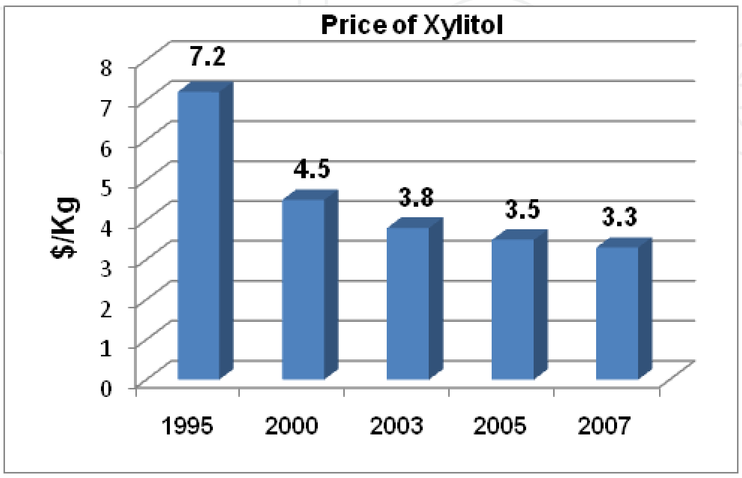

Figure 2. Xylitol price profile from 1995 to 2007 (Source: adapted from reference [109]).

4.3.5. Ethanol

Currently, the world has the prospect of a significant increase in demand for ethanol. The use of this fuel is concentrated on a global scale in power generation, in its mixture with gasoline or simply dehydrated, being a considerable product in the global energy matrix [110].

The first generation ethanol production consists in conversion of hexose sugars to ethanol, and it is relatively simple and usually performed in three steps: acquisition of fermentable sugars, fermentation of sugars by microorganisms and separation and purification of ethanol, usually carried out by distillation, rectification and dehydration [111]. Microorganisms such as *Saccharomyces cerevisiae* consumes directly the sucrose present in sugarcane juice producing ethanol. However, in the long scenario, the use of juice or molasses to produce ethanol will not be able to supply the increasing demand.

Biofuels from renewable sources, such as second generation ethanol production from lignocellulosic materials (bagasse and straw), may represent a sustainable alternative to environmental and social problems caused due to the extensive use of fossil fuels [112]. The process for second generation ethanol requires three steps: pretreatment of lignocellulosic materials, to make the hemicellulose sugars and cellulose more accessible, fermentation of sugars and separation and purification of ethanol [111]. Although it is an eminent perspective, the development of this technology requires some additional challenges. The production of ethanol from lignocellulosic biomass can increase the productivity of ethanol per hectare of sugar cane planted [113], without increasing the cultivated area in the same proportions, not competing with food production for land use [112].

S. cerevisiae is the most common microorganism used for ethanol production from hexose sugars, but it is unable to produce ethanol from pentoses such as xylose. Among the microorganism that can assimilate pentose sugars such as xylose, yeasts have shown more ethanol yield and productivity than bacteria and fungi [114]. There are some naturally yeast which ferments xylose to ethanol, among them, *Pichia stipitis* [116] and *Candida shehatae* [117] are the most employed in bioprocess.

Considering the process for production of second generation ethanol, sugarcane bagasse is reported as one of most used lignocellulosic materials, and among the microorganisms used for xylose conversion, *P. stipitis* yeast (taxonomic classification has been changed to *Scheffersomyces stipitis* [118]) is widely used. For example, from sugarcane bagasse hemicellulosic hydrolysate, Canilha et al. [119] reported 7.5 g/L, 0.30 g/g and 0.16 g/L.h of ethanol production, yield and productivity, respectively, using hydrolysate treated with ion exchange resins as a medium of fermentation for ethanol production by *P. stipitis* DSM 3651 while Hande et al. [120] obtained 0.45 g/g using hydrolysate treated by neutralization and activated charcoal adsorption as a medium of fermentation for ethanol production by *Pichia* strain BY2. Other yeasts can be found in studies for ethanol production from sugarcane hemicellulosic hydrolysate. For example, Chandel et al. [121] observed maximum ethanol yield (0.48 g/g) from ion exchange detoxified hydrolysate followed by use activated charcoal, by *C. shehatae* NCIM 3501 and Cheng et al. [122] obtained 19 g/L ethanol, yield of 0.34 g/g and productivity of 0.57 g/L.h when used a batch culture with pretreated hydrolysate as substrate for *Pachyso-*

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len tannophilus DW06. For sugarcane straw, the ethanol production is only from cellulosic fraction. For example, Krishnan et al. [4] verified an ethanol production about 34–36 g/L using the recombinant *S. cerevisiae* (424A LNH-ST) from the bagasse and straw pretreated by ammonia fiber expansion method (AFEX). Sindhu et al. [123] observed the ethanol production of 11.365 g/L using *S. cerevisae* yeast from leaves pretreated with dilute acid hydrolysis followed by enzymatic saccharification with cellulases.

Regarding the world ethanol scenario, a regular increase in the production has been observed (Figure 3). The Americas are the largest producer continent of ethanol. The United States of America is the largest producer country of ethanol with production levels over 51 billion liters (13.5 U.S. gallons) in 2011 [124].

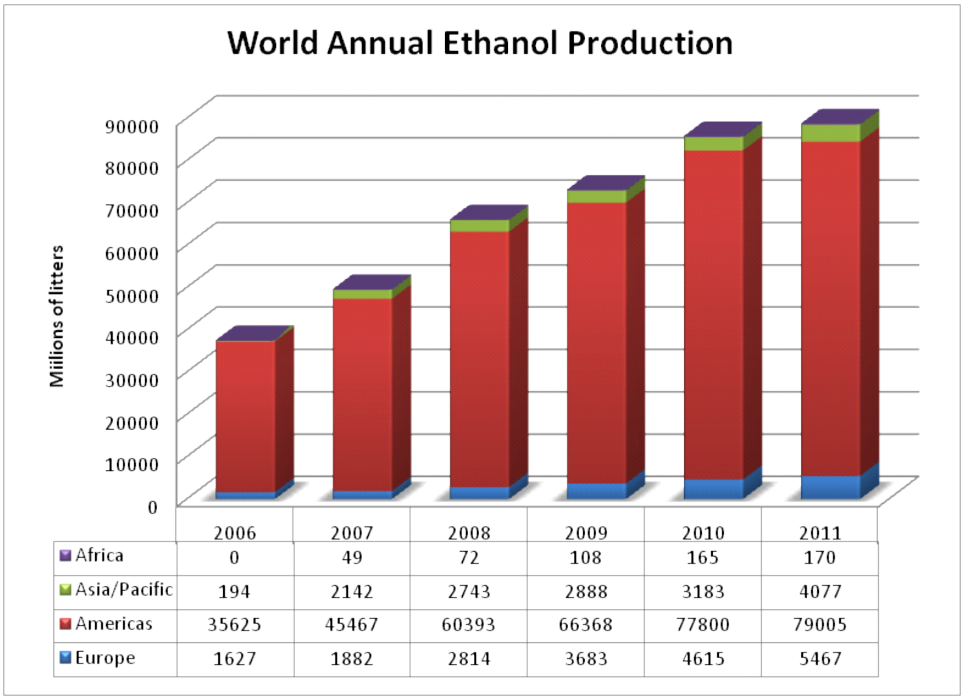

Figure 3. World Annual Ethanol Production since 2006 (Source:[125]).

4.3.6. Butanol

Biobutanol, a four carbon primary alcohol (butyl alcohol-$C_4H_{10}O$), is second generation alcoholic fuel with a higher energy density and lower volatility as compared to ethanol in addition to its existing applications as a solvent [126, 127]. The primary use of butanol is as an industrial solvent in the manufacturing of products such as lacquers and enamels. Butanol can be used directly in any gasoline engine without modification and/or substitution, because it has several similar characteristics to gasoline, besides being compatible with ethanol blending may improve the blending of gasoline with ethanol [128]. It can be produced through processing of domestically grown crops, such as corn and sugar beets, and other biomass residues [128].

Production of butanol by using fermentation to replace the chemical process depends largely on the availability of inexpensive and abundant raw materials and efficient bioconversion of these materials. The producers strains of biobutanol which have been extensively studied are *Clostridium sp.* [126, 127] and genetically engineered *E. coli* [129, 130]. Studies to determined the recovery of biobutanol from fermentation broth (dry corn and wet corn milling) whey permeate and molasses) by distillation showed that it was not economical when compared with butanol derived from the current petrochemical route [131]. The use of lignocellulosic substrates in combination with developed process technologies is expected to make the production of biobutanol economically viable [132].

4.3.7. Butanediol

2,3-Butanediol (2,3-BDL), also known as 2,3-butylene glycol, is a valuable chemical feedstock because of its application as a solvent, liquid fuel, and as a precursor of many synthetic polymers and resins. One of its well known applications is the formation of methyl ethyl ketone, by dehydration, which can be used as a liquid fuel additive [8].

Butanediol is produced during oxygen-limited growth, by a fermentative pathway known as the mixed acid-butanediol pathway [133]. The 2,3-BDL pathway and the relative proportions of acetoin and butanediol serve to maintain the intracellular NAD/NADH balance under changed culture conditions. All of the sugars commonly found in hemicellulose and cellulose hydrolysates can be converted to butanediol, including glucose, xylose, arabinose, mannose, galactose, and cellobiose. The theoretical maximum yield of butanediol from sugar is 0.50 kg per kg. With a heating value of 27,200 J/g, 2,3-BDL compares favorably with ethanol (29,100 J/g) and methanol (22,100 J/g) for use as a liquid fuel and fuel additive [134]. Hexose and pentose can be converted to 2,3-BDL by several microorganisms including *Klebsiella* [135], *Aeromonas* [136], *Bacillus* [137], *Paenibacillus* [138], *Serratia*, *Aerobacter* [139] and *Enterobacter* [140].

4.3.8. Biopolymers

The use of plastics is consistently increasing in the society due to its advantages such as low cost and durability, and the replacement of conventional materials such as paper and glass [141]. However, these materials have xenobiotic and recalcitrant nature, having an extremely long degradation rate [142, 143]. Besides its slow degradation, the accumulation of plastic is a major risk to marine animals. When is landfilled, is more difficult to occurs the process of decomposition and when it is incinerated, causes the release of several toxic compounds [144]. Due to the increasing demand of plastics and its incorrect disposal, these materials have become a major environmental problem. An alternative to trying to solve this rising problem is the replacement of conventional plastics for biodegradable plastics. Biodegradable plastics are natural biopolymers that are synthesized and catabolized by microorganisms and are made from renewable resources and do not lead to the depletion of finite resources [145, 146]. Among bioplastics, polyhydroxyalkanoates (PHA) and polylactates (PLA) got significant attraction. The PHA's are typically accumulated by bacterial via intra or extracellular while PLA is produced by polymerizing lactic acid via microbial fermentation [147].

For replacement of the conventional plastic, biodegradable plastic is a feasible option. However, it is necessary that the price of biopolymers should be competitive [148]. The cost of production is directly linked to the type of microorganism and the substrate employed. The strain used should have a high specific growth rate, using low cost substrates and a high conversion factor of substrate in PHA [144]. The selection of the proper raw material for biopolymer production has an additional impact on the ecological pressure of the entire process [148]. Renewable sources of polymeric materials offer an answer for sustainable development of economically and ecologically attractive technology [149, 150].

Sugarcane biomass represents an enormous reserve of renewable carbon source, which has the potential to be utilized as a feedstock for the production of biodegradable polymers. For instance, using sugarcane bagasse hydrolysate, Yu and Stahl [151] investigated the simultaneous detoxification and PHA production by the bacterium *Ralstonia eutropha* and accumulated PHA at a rate of 57 wt% of cell mass despite the large index of inhibitors. Silva et al. [152] studied the biopolymer production by *Burkholderia cepacia* IPT 048 and *B. sacchari* IPT 101 from sugarcane bagasse hydrolysate and obtained polymer contents and yields reached, respectively, 62% and 0.39 g/g with strain IPT 101 and 53% and 0.29 g/g with strain IPT 048.

4.3.9. Single cell protein

To create a balance between food versus fuel production from lignocellulosic residues, adequate land use, judicious usage of grain and corn/cane crop residues is essential [153]. Mathews et al. [153] presented a sugarcane 'feed+fuel' biorefinery model, which produces bioethanol and yeast biomass, a source of single-cell protein (SCP), that can be used as a high-protein animal feed supplement. The yeast SCP, which is synthesized as a part of the process of producing cellulosic bioethanol from sugarcane can be used as a supplement for grass in the feed of cattle grazing on pasture and thereby potentially release land for increased sugarcane production, with minimal land use change effects.

The production of SCP by growing microorganisms on organic wastes and its use in animal feed has a long history. Protein as an animal feed supplement has long been viewed as a potentially very significant development, with much discussion devoted to the topic of microbial SCP since the 1970s. The grounds for the intense interest in SCP is that feedstocks, in the form of agricultural and organic wastes are plentiful, and the rate of growth of microorganisms producing SCP is prodigious. Whereas a soybean crop is harvested after 1 season of growth, microorganisms double their cell mass within hours [154]. According to Tanaka et al. [155] the production of single-cell protein (SCP) from lignocellulosic materials needs four steps: (1) physical and chemical pretreatments; (2) cellulase production; (3) enzymatic hydrolysis; and (4) assimilation or fermentation of holocellulose. For each step the following topics need to be considerate: (1) effect and mode of action of each pretreatment; (2) optimization of culture media and operating conditions, and application of mutation, protoplast fusion and gene recombination; (3) elucidation of kinetics of cellulase reaction, and methods of immobilization, stabilization and recovery of cellulases; and (4) examples of SCP production by several types of cultivation and treatment of lignin. According to Zadrazil et al. [156] in order to convert a lignocellulosic material to obtain a more nutritive product, it is necessary to choose a microorganism or a microbial complex capable of synthesizing proteins with high nutritional value and, in the case of use of a substrate that has not been subjected to a previous hydrolysis step, able to degrade selectively the lignin present in the substrate. The lignocellulosic wastes can be fermented directly or they can be previously hydrolyzed chemically. Several reports have shown the application of substrates chemically pre-hydrolyzed for rapid protein enrichment by microbial fermentation. For example, Pessoa et al [157] hydrolyzed sugarcane bagasse using diluted sulphuric acid and the hydrolysate was fermented with *Candida tropicalis*. This process resulted in a 31.3% increase in protein content after 5 days of fermentation. However, for non-ruminant animals, which are not able to metabolize the natural fibers that comprise the bulk of lignocellulosic wastes, the bioconversion process must aim to transform these fibers into digestible components such as protein and sugars (mono- and disaccharides) as well as vitamins and minerals.

5. Conclusion and future recommendations

Sugarcane bagasse (SB) and straw (SS) constitute a sizeable fraction of agro-residues in many countries. Brazil is the largest producer of sugarcane residues in the world. Hemicellulose, in both raw materials, is an important fraction and could be a sustainable alternative for the production of second generation ethanol, industrial enzymes, food/feed and fine chemicals such as lactic acid, succinic acid, etc. It can be easily converted into simple sugars by thermochemical processes and the resultant sugar solution after conditioning and detoxification, can be converted into the aforementioned products by biotechnological routes. Alterations in thermochemical processes such as implication of counter-current, plug-flow, percolation and shrinking-bed reactors could be helpful to maximize the sugars recovery with minimum inhibitors generation. There are several promising detoxification strategies available which remove the inhibitors from hydrolysates. The detoxified sugar solution can be converted into valuable products including second generation ethanol by appropriate microorganisms under batteries of fermentation. Laboratories based research progress has clearly showed that it is quite possible to convert hemicellulose into commercially significant products with desired yields and productivities. However, it is necessary to build a robust process to be employed at industrial scale. Bio-products derived from hemicellulose of SB/SS have shown potential to replace chemically synthesize products. Owing to this, bio-industrial companies offer numerous opportunities to develop unique functionality and marketing benefits from the products derived from hemicellulose of SB/SS creating long term sustainability and green environment.

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