

1 **A review of sugarcane bagasse for second-generation bioethanol and biopower**
2 **production**

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11 **Abstract**

12 Sugarcane bagasse is a large-volume agriculture residue that is generated on a ~540
13 million metric tons per year basis globally^{1, 2} with the top three producing countries in
14 Latin America being Brazil (~181 million metric ton yr⁻¹),³ Mexico (~15 million metric
15 ton yr⁻¹)⁴ and Colombia (~7 million metric ton yr⁻¹),⁵ respectively.⁶ Given sustainability
16 concerns and the need to maximize the utilization of bioresources, the use of sugarcane
17 bagasse is receiving significant attention in biorefining applications, as it is a promising
18 resource for the conversion to biofuels and biopower. This review will provide a
19 comprehensive review of bagasse, its chemical constituents and on-going research into its
20 utilization as a feedstock for cellulosic ethanol and electricity generation.

21
22 Keywords: sugarcane bagasse; bioethanol; biopower; second-generation

23 **1 Introduction**

24 In the past few decades, the high consumption of fossil fuels has led to an increase use of
25 difficult to recover petroleum reserves, which have heightened environmental concerns
26 along with energy security issues. These issues, in addition to global climate change due
27 to greenhouse gas emissions, have led researchers to explore alternative fuels based on
28 sustainable bioresources. Agro-energy crops and plant residues are two of the most
29 promising low-cost, sustainable biomaterials for biofuel and power generation.

30
31 First generation bioethanol has been widely used for vehicle fuels, lowering net carbon
32 dioxide emissions compared to fossil fuels. However, the increasing demand for ethanol
33 requires high feedstock production and an increase in land usage. This could impact
34 biodiversity and competition with food crops, yielding in increases in food prices in
35 addition to limited economic growth. Second generation biofuels could avoid many of
36 these concerns since it relies on nonfood bioresources, such as lignocellulosics. These
37 lignocellulosic materials are relatively inexpensive and available in large quantities. One
38 of the most commonly examined lignocellulosic materials for second-generation ethanol
39 production is sugarcane bagasse.⁷⁻¹⁰

40
41 Sugarcane is a versatile plant grown for sugar production, and it's major by-product is

1 bagasse.¹¹ Bagasse is the residue obtained after sugarcane is milled for juice extraction.
2 In sugarcane production, the bagasse retrieved from crops is roughly 27-28 dry weight %
3 of plant biomass.^{1, 12} It is a highly heterogeneous material that consists roughly of 20-30%
4 lignin, and 40-45% cellulose and 30-35% hemicellulose¹³ with limited amounts of
5 extractives and ash. Its composition makes it a promising feedstock for second-generation
6 biofuel production. Similar to other lignocellulosic materials, sugarcane bagasse has low
7 nutritional value, which precludes concerns about the food vs. fuel debate. A variety of
8 species of sugarcane, *Saccharum spp*, are grown in Latin America, which leads it to
9 numerous differing resources of bagasse, which is generally underutilized. Furthermore,
10 bagasse represents approximately 0.3 metric ton for every 1 metric ton of sugarcane¹
11 grown and is often considered a waste stream. A comprehensive understanding of
12 bagasse chemical constituents and its physical and chemical characteristic changes
13 associated with the bioconversion process from biomass to biofuel is necessary in order
14 to amplify bagasse as a renewable source. The delicate problem for second-generation
15 biofuel production is the optimization of pretreatment technologies, which may include
16 hydrothermal, dilute acid, steam explosion, alkaline and organosolv. Although it is costly,
17 the pretreatment of bagasse has been reported to facilitate up to 90% conversion of sugars
18 to ethanol compared to 20% without pretreatment for acid hydrolysis.¹⁴
19

20 **2 Sugarcane in Top Producing Countries**

21

22 Originally from Asia, sugarcane can be found in most tropical and subtropical climates.
23 As of 2013, the world sugarcane production accounted for approximately 1900 million
24 metric ton with the top countries located in Latin America and Asia.^{6, 15} Brazil being first
25 (~40%), India second (~19%), China third (~7%), Thailand fourth (~5%), Mexico sixth
26 (~2.5%) and Colombia seventh (~1.5%) in global production rankings. Argentina has
27 increased its average sugarcane growth over the last few years and now contributes to
28 1.1% of world production.¹⁶ Table 1 shows the most recent approximate sugarcane crop
29 production in different countries.
30

31 The majority of Colombian sugarcane plantations are located around the Cauca River
32 Valley, and grow all year round with the potential to produce around 954 000 L d⁻¹ of
33 ethanol from sugarcane juice.¹⁷ This would represent the second largest ethanol producer
34 in Latin America with all bioethanol coming from sugarcane.^{17, 18} Sugarcane plantation in
35 Cauca River Valley in Colombia is harvested on around 200,000 ha of land and it is
36 estimated that the country can potentially generate 3.8 million L d⁻¹ of fuel ethanol by
37 2020.¹⁹ In Mexico, sugarcane is harvested through manual cutting once a year in a period
38 between December and May.²⁰ Although Mexico is known for sugarcane crops,
39 sugarcane yields decreased from 72 to 64 metric ton ha⁻¹ annually in the last decade,
40 which was attributed primarily to climate change.²¹ Cuba used to be one of the largest
41 exporters of sugar in the world with its main export market being the United States until
42 the commercial trade blockage in the early 1960s. Cuba turned to the Soviet Union and
43 Eastern European countries for trade but eventually lost these markets in 1991 due to the
44 collapse of communism. Since then sugarcane production has significantly declined from
45 80 million metric ton yr⁻¹ to 24 million metric ton yr⁻¹ from 1991 to 2004. In 2005 it
46 declined to 11.6 million metric ton yr⁻¹ following the trend observed in the preceding

1 years.²² However, Cuba has a great potential for sugarcane production and energy derived
2 from sugarcane agricultural residues is under review.²³ Argentina, on the other hand, has
3 its production limited to the northern, fertile, warm crop areas. Argentina typically uses
4 the flat region in northern parts of the country, typically referred to as the pampas, due to
5 the very fertile land and moderate warm climate that permits year round crop growth.
6 Production is located on 320,000 ha of land.¹⁶ Brazil is the leading country in sugarcane
7 crop production with an estimated 55% of sugarcane transformed into ethanol, which
8 yields an average of about approximately 68 liters per metric ton of sugarcane.¹⁸ As of
9 2013, India is the second biggest producer of sugar in the world (27%).²⁴ Its cane is
10 planted throughout three seasons (spring, summer and fall) in the northwestern region,
11 with fall's duration being 12-14 months and its cultivation yielding higher amounts of
12 cane and sugar recovery.²⁵ Thailand has been growing its sugarcane productivity
13 significantly since 2004, a growth average of 53% from 2004 to 2013. This growth has
14 placed Thailand as the fourth largest producer of sugarcane in the world with 51
15 functioning mills, 100 thousand farmers on 1.6 million ha of land.¹⁵

16 **3 Sugarcane Agricultural Characteristics**

17 Sugarcane belongs to the family *Poaceae* of the genus *Saccharum*. Its taxonomy and
18 nomenclature have been difficult to record over the years but essentially the genus
19 *Saccharum* (*S.*) consisting of six species known as *S. officinarum*, *S. spontaneum*, *S.*
20 *robustum*, *S. sinense*, *S. barbieri*, and *S. edule*, and some of its agricultural characteristics
21 are shown in Table 2. Among the sugarcane species, *S. officinarum* contains high sucrose
22 however it has poor resistance to disease. *S. spontaneum* is highly adaptable and may
23 grow in various altitudes in tropical and subtropical climates. Due to the susceptibility to
24 some diseases found in the most common specie (*S. officinarum*), breeding methods of
25 sugarcane have been developed. In the last three to four decades, one of the major
26 contributions of breeding sugarcane has been to produce higher sugar yield. Hence there
27 have been modification in sugarcane chemical composition, for example the breeding
28 varieties from 2011 had higher lignin and ash content than that of 2009, potentially
29 leading to lower glucose yield.²⁶ Currently, there are numerous genetic breeding efforts
30 such as simple sequence repeat and marker-assisted selection²⁷ where hybrid sugarcane
31 plants have been derived from the crossing of *S. officinarum* and *S. spontaneum* for
32 commercial purposes.^{6,28}

35 **3.1 Sugarcane Processing**

36 After growing for 12-16 months, sugarcane is cut for collection. Manual harvest involves
37 burning the crop for collection, which facilitates the cutting process. This collection
38 method is still used although many companies are projected to utilize mechanized
39 harvesting of green sugarcane due to worker safety and environmental concerns.²⁹
40 Mechanical cutting does not involve burning the cane before collection, however it
41 presents some operational challenges.²⁹ It has been highly adopted since it replaces the
42 labor of up to 100 workers per farm in manual harvest.³⁰ In most recent studies, the state
43 of Sao Paulo in Brazil used the green-harvest system for the cane, which accounted for
44 65.2% of the harvesting method and is expected to banish the burning harvest by 2029.³¹

1 Mechanical cutting does not permit the cane to be washed because the loss of sucrose is
2 higher; hence mills use a dry wash process (i.e., jets of air). The chopped sugarcane is
3 then placed in a shredder with the objective of opening the cells containing sugars and
4 facilitating the sucrose extraction process. Grinding is an extraction process, which
5 results in juice extraction and the agriculture residue, bagasse. Usually the first batch of
6 juice extracted goes to sugar manufacturing and about 55%³² goes to ethanol production.
7 Sugarcane is usually cultivated for six years before replanting.²⁰ Sugarcane maturity,
8 harvesting method, type of soil and efficiency of equipment used for the extraction
9 process may affect the composition of sugarcane bagasse.

10

11 **4 Pretreatment of sugarcane bagasse**

12 The conversion of bagasse to biofuels has been actively studied using both the biological
13 and thermal platform. One of the most promising pathways is second-generation
14 cellulosic ethanol as summarized in Figure 1. Pretreatment is one of the major steps in the
15 biological conversion of bagasse to bioethanol as it reduces its recalcitrance. It can be
16 accomplished using biological, chemical, physical, or various combinations of these
17 treatments. The reduction in recalcitrance has been attributed to several factors including
18 changes in the interactions of hemicellulose, cellulose and lignin, increases in cellulose
19 accessibility, removal of lignin-carbohydrates complexes and possible reductions in
20 cellulose crystallinity in the plant cell wall. These effects increase sugar yields from
21 cellulose thereby increasing ethanol fermentation yields provided fermentation inhibitors
22 are managed. A variety of pretreatments have been used in recent studies for sugarcane
23 bagasse as summarized in Table 3.

24

25 Steam explosion is a physico-chemical pretreatment prevalently used in sugarcane
26 industry due to its low environmental impact and cost.^{8,33} It is a process in which the
27 lignocellulosic materials in sugarcane bagasse are exposed to hot steam and pressure
28 followed by explosive decompression of bagasse that results in lignin rearrangement due
29 to partial hemicellulose hydrolysis and lignin solubilization due to high temperatures.³⁴
30 Enzymatic hydrolysis is also facilitated by changes in cellulose crystallinity and degree of
31 polymerization caused by steam explosion.³⁵

32

33 Hot water pretreatment of bagasse is environmentally beneficial as there is reduced
34 deterioration of polysaccharides, and consequently lower inhibitor generation.³⁶ The
35 disadvantage to this pretreatment is the high volume of water consumption and energy
36 costs. This method generally employs temperatures ranging from 120-230 °C for 1-80
37 min and may recover 55 to 84% of hemicelluloses.³⁷⁻³⁹ However, shorter periods of time
38 ranging from 1-20 min and temperatures lower than 200°C are more commonly used so
39 to minimize changes in lignin and cellulose.

40

41 The extrusion process is a physical pretreatment method that utilizes irradiation, and
42 comparable to other treatments, targets the degradability of lignocellulosic materials for
43 the enhancement of enzymatic hydrolysis. Such irradiation treatment for sugarcane
44 bagasse comes in the form of microwaves, ultrasound and gamma rays.^{33, 40} Gamma rays
45 increase cellulose crystallinity as well as surface area, whereas microwave and ultrasound
irradiation, given adequate conditions, decrease crystallinity of cellulose.^{33, 40, 41}

1 Acid hydrolysis is efficient in breaking down hemicellulose and maximizes sugar yield
2 from bagasse. It is a commercial method adopted by many researchers however the cost
3 is claimed to be higher than that of liquid hot water pretreatment.³⁷ Dilute acid and
4 concentrated acid are two types of acid hydrolysis. Dilute acid usually uses less than 10%
5 acid concentration while concentrated acids is greater than 10%.⁴² Acids such as sulfuric
6 and phosphoric acid help to solubilize hemicelluloses and transform them into
7 fermentable sugars.⁴³ In sugarcane bagasse pretreatment using sulfuric acid with 0.5%
8 concentration at 121°C during 60 min yielded 24.5 g L⁻¹ of total sugar after cellulose
9 hydrolysis.¹³ The use of hydrochloric acid has also been studied at 130°C, 1.25% HCl
10 concentration for 10 min resulting in 76.6% sugar release after 72 h of enzymatic
11 hydrolysis.⁴⁴

12 Organosolv pretreatment of sugarcane bagasse mainly utilizes ethanol (EtOH) and water
13 as an organic solvent mixture.³³ The α -aryl ether linkages of lignin are reactive under
14 these conditions and are hydrolyzed and solubilized. This process is convenient for small
15 mills because of its ease of recovery method and sulphur free discharge³⁷ but remains
16 costly.³³ When bagasse was mixed with 60:40 EtOH/water with 5% dosage of acetic acid
17 at 190°C for 45 min, sugar yield reached 85.4% after 72 h of enzymatic hydrolysis.⁴⁵

18 Alkaline pretreatments of bagasse promote the separation of cellulose and are efficient in
19 the removal of lignin. The alkali usually causes a swelling in the biomass, which allows
20 for the decrease in cellulose crystallinity. In contrast to other pretreatments, this particular
21 process works at low reaction pressures, temperatures and concentration, which can be
22 linked to reduce fermentation inhibitors and low cost.⁴⁶ However, its biggest
23 disadvantage is associated to the difficulty of alkali recovery. A sodium hydroxide
24 pretreatment (i.e. 110°C for 1 h and 0.18% of NaOH) of bagasse has been shown to result
25 in 77.3% sugar release after 72 h of enzymatic hydrolysis.⁴⁴

26 Ionic liquids are salts composed of anions and cations of organic compounds, which are
27 poorly organized making them have a melting point below 100 °C.⁴⁷ These solvents have
28 great thermal stability, non-volatility⁴⁸ and are exceptional catalysts for the
29 delignification of bagasse.⁴⁹ Among different ionic solvents, most commonly used for
30 sugarcane bagasse is 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]), which has been
31 reported to be very effective in dissolving cellulose.⁵⁰ Other solvents used for
32 pretreatment of bagasse that have been reported include 1-butyl-3-methylimidazolium
33 acetate ([Bmim][Ac]), 1-allyl-3-methylimidazolium chloride ([Amim][Cl]), 1-butyl-3-
34 methylimidazolium chloride ([Bmim][Cl]) and 1,3-dimethylimidazolium dimethyl
35 phosphate ([Mmim][DMP]).^{48, 51, 52} These ionic liquids can remove up to 60% of lignin in
36 sugarcane bagasse along with decreasing the crystallinity of cellulose fibers.⁵³ It has been
37 reported that a 1:20 solution of bagasse to ([Mmim][DMP]) at 120 °C for 120 min
38 resulted in 70.38% of sugar conversion after 48 h of enzymatic hydrolysis.⁵²

39 **5 Sugarcane Bagasse Constituents and Characteristics**
40

41 **5.1 Cellulose Structure**

1 Cellulose is a homopolysaccharide chain composed of anhydroglucose units linked by β -
2 (1,4)-glycosidic bonds (Figure 2) which form a crystalline structure due to extensive
3 intra- and intermolecular hydrogen bonds that facilitates its aggregation into fibrils.⁵⁴ The
4 average molecular weight of sugarcane bagasse cellulose ranges from 157800-168400g
5 mol⁻¹⁵⁰ and the size of its cellulose fibers range from 1.0-1.5 mm.⁵⁵ A cellulose unit,
6 known as elementary fibril, can be coated with other non-cellulosic polysaccharides to
7 form micro-fibrils, which can then be cross-linked by hemicellulose matrices to form
8 macro-fibrils, which creates resistance to chemical and enzymatic degradation.

9 Degree of polymerization pertains to the number glucose units in the molecular polymer
10 and it can influence the effectiveness of enzymatic hydrolysis. The average degree of
11 polymerization (DP_w) in sugarcane bagasse cellulose ranges from 974-1039.⁵⁰ DP_w
12 varies under different cellulose isolation methods and is dependent on the intrinsic
13 viscosity (η). Intrinsic viscosity is the measure of volume occupied by the macromolecule
14 and their ability to disturb flow (Table 4).⁵⁶ When sugarcane bagasse was subjected to
15 delignification and potassium hydroxide isolation the DP_w was 1406.5 while the
16 combination of acetic and nitric acid lowered DP_w to 822.5, indicating that the acetic and
17 nitric acid mixture degrades the macromolecule of cellulose more than potassium
18 hydroxide.⁵⁶

19 The predominant polymorph of cellulose is known as cellulose I and can be detected
20 through X-ray diffraction (XRD) and solid state cross polarization magic-angle spinning
21 carbon-13 nuclear magnetic resonance (CP/MAS ¹³CNMR) spectroscopy.⁵⁶ XRD is one
22 of the most commonly used techniques for crystallinity index (CrI, %) analysis^{57, 58} and it
23 showed that the untreated bagasse contains an average CrI of 56.7%. Table 4 shows the
24 CrI of untreated commercial sugarcane bagasse. This index is frequently used to
25 determine relative quantity of crystalline material present in sugarcane bagasse. CP/MAS
26 ¹³CNMR has shown to be extremely resourceful in the morphological modifications
27 analyzed in cellulose throughout hydrolysis, where the 64.8 ppm chemical shift
28 corresponds to the C-6 crystalline cellulose signal and this is ratioed to 62.4 ppm signal
29 for the C-6 amorphous of cellulose.⁵⁶

30 5.2 Hemicellulose Structure

31 Hemicellulose is a heteropolysaccharide of low molecular weight. It averages 7380g mol⁻¹
32 in bagasse.⁵⁹ Sugar composition of hemicellulose in bagasse is primarily galactose
33 (11.5-39.9%), xylose (15.5-28.9%) and glucose (17.5-50.5%) with smaller amounts of
34 arabinose (5.35-14.31%), mannose (0.0-14.0%), rhamnose (2.5-10.6%) and uronic acids
35 (1.0-2.3%).⁶⁰ Hemicellulose in sugarcane bagasse is composed of β -(1 \rightarrow 4)-xylo-pyranose
36 backbone, having about 200 β -xylopyranose residues linked by 1,4-glycosidic bonds,
37 glucomannans and galactomannans, xyloglucans, β -glucans and small amounts of uronic
38 acids.^{61, 62} The degree of branching in hemicellulose is given by the arabinose/xylose
39 ratio; hence, the lower the ratio the higher the degree of polymerization and likewise the
40 higher the ratio the shorter the polymer chain.⁶⁰ Values for the arabinose/xylose ratio are
41 approximately 0.2 for bagasse.^{59, 63} Hemicellulose is linked to lignin by covalent bonds,
42 whereas the linkage between hemicellulose and cellulose is by the way of hydrogen
43 bonds, which integrate easily with one another creating stability and flexibility.⁶⁴ In sugar

1 cane the hemicellulose content is found to be low, on average 19.90%,⁶⁵ compared to that
2 of sugarcane bagasse which is approximately between 30-35%.¹³ There are many
3 methods of extraction of hemicellulose such as autohydrolysis,⁶⁶ active oxygen species
4 (oxygen and hydrogen peroxide) and solid alkali,⁶¹ and alkaline peroxide.^{67, 68} In
5 general, isolation comes from multiple alkaline extractions causing the cleavage of ester
6 linkages and extracting the hemicellulose from the lignocellulosic matrix. Potassium
7 hydroxide and sodium hydroxide with hydrogen peroxide pretreatments for hemicellulose
8 isolation have shown high values for xylose, 83.1-84.6 and 85.02%, respectively.^{59, 68} In
9 comparison, dewaxed and distilled water, and water with solid alkali precooking resulted
10 in much lower xylose yields, 55.20 and 57.43%, respectively (Table 5).^{59, 61}

11 Structural changes in bagasse hemicellulose after isolation are typically analyzed using
12 FTIR and ¹³C NMR.^{59, 61, 63} FTIR has indicated complete rupture of ester bonds when
13 under alkali pretreatment conditions (10% KOH with 20°C, 35°C and 50°C).⁶⁸ ¹³C NMR
14 was able to detect strong signals indicating the presence of 1,4-linked β -D-Xylp units and
15 the 4-O-methoxyl group of glucuronic acid residues in xylan.^{59, 61} It was concluded that
16 β -D-Xylp units was the main component in bagasse hemicellulose.⁶¹

17

18 5.3 Lignin Structure

19 Lignin, the most abundant aromatic polymer, is an amorphous three-dimensional
20 phenolic biopolymer. The biosynthesis of lignin could be considered to arise from
21 polymerization of three types of phenylpropane units as the monolignols: *p*-coumaryl,
22 sinapyl and coniferyl alcohols that allows for the rigid form (Figure 3). These
23 monolignols can then give rise to the p-hydroxyphenyl (H), syringyl (S), and guaiacyl
24 (G) lignins units.⁵¹ Lignin in bagasse has a molecular weight average range of 507-
25 3973 mol g⁻¹.⁶⁹ Lignin in sugarcane is extremely low, average of 2.37%⁷⁰ and 4.16%⁶⁵,
26 compared to ~25% found in sugarcane bagasse. Additionally, it has been reported that
27 lignin content in sugarcane genotype IACSP04-627 to be 8.12% and IACSP04-065 to be
28 4.32%.⁷¹ Table 6 shows the lignin content in different sugarcane bagasse.

29 Lignin affects most pretreatment methods as well as enzymatic hydrolysis, thus multiple
30 studies have been made for structural information of lignin, such as ionic liquid,
31 ammonia, dilute acid, etc.^{51, 56} Isolation methods for bagasse such as pyrolysis coupled to
32 gas chromatography-mass spectrometry (Py-GC/MS) showed that both coumaric and
33 ferulic acid play an important role in the structure of bagasse accounting for 63% lignin
34 compounds.⁷²⁻⁷⁴ The γ -OH acylation of lignin side-chain by *p*-coumarates indicating that
35 *p*-coumarates are primarily attached to the lignin polymer. Ferulates however, showed
36 acylation of arabinosyl residue from arabinoxylan chains revealing that ferulates are
37 generally linked to carbohydrates in the cell-wall.⁷² Ionic liquid and hot water
38 pretreatment both hydrolyzed the β -O-4 inter-unit links.^{51, 69} Different methods for lignin
39 isolation in sugarcane bagasse were efficient for lignin extraction processes showing the
40 cleavage of β -O-4' linkages such as: dilute acids followed by steam explosion and
41 ethanol washing, as well as alkali followed by steam explosions.⁶⁹ Proton, carbon,
42 phosphorus and two-dimensional heteronuclear single quantum coherence Nuclear
43 Magnetic Resonance (¹H, ¹³C, ³¹P and 2D HSQC NMR) are primarily used to identify the
44 functional groups in the isolated lignin structure.^{51, 69} An assessment of various hydroxyl

1 groups in organosolv lignin, with results S-OH: 0.58 mmol g⁻¹, G-OH:0.47, H-OH:0.53
2 among others, can be obtained using ³¹P NMR spectra.⁷⁵ The 2D HSQC NMR is able to
3 approximately determine the carbohydrate complexes of lignin that ¹H, ¹³C and ³¹P NMR
4 are not able to detect due overlapping in signals.⁵¹ Isolated lignin from sugarcane bagasse
5 was reported to be composed of 83% of β -O-4' links, alkyl-aryl ether bonds, and very
6 few quantities, 6% of β -5, phenylcoumarans; and, molar ratio of H:G:S was confirmed to
7 be 2:38:60 respectively,⁷² concluding bagasse is S-rich (Table 7). According to del Río *et*
8 *al.*⁸ the lignin of bagasse is derived from mature stem and therefore is rich in syringyl (S)
9 lignin, which is present in mature tissue. The conclusions indicated that lignin from
10 sugarcane bagasse is mainly composed of β -O-4' alkyl-aryl ether linkages.

11 **5.4 Ash and extractives**

12 The by-product of sugarcane bagasse after it is used for fuel in plants cogeneration
13 systems is bagasse ash. Sugarcane bagasse ash is black in color and contains 2.39g cm⁻³
14 of particle density with irregular shaped particles.⁷⁶ It contains about 87.8% of sand with
15 particles sizes greater than 63 μ m, 11.50% of slit with particles sizes ranging from 2 to
16 63 μ m, 0.7% of clay with less than 2 μ m and 10.32% of organic matter.^{76, 77} In Brazil,
17 sugarcane bagasse ash generation was estimated to be approximately 2.5 million tons per
18 year and is discarded primarily as soil fertilizer.⁷⁷ Economical and technological
19 development for the application of ash have grown in the past few years. Ash from
20 bagasse is rich in silica and hence may be used for recycling purposes such as ceramic
21 raw material, additive to cement, concrete and fine aggregate in mortars.^{77, 78} XRD has
22 been used to determine the inorganic oxide content in bagasse ash (Table 8).⁷⁶⁻⁷⁸

23 Extractives in sugarcane bagasse range from 2.3-10.5% of total chemical composition.⁷⁹
24 These extractives are hydrophobic and can be fatty acids, waxes, and proteins, among
25 others.^{79, 80} Research has reported that about 0.9% of acetone extractives contained about
26 140 mg k⁻¹ of *n*-fatty acids, 700 mg k⁻¹g of *n*-aldehydes and 330 mg k⁻¹ of *n*-fatty
27 alcohols in bagasse.⁷⁹ For chemical analysis purposes, extractives are usually removed
28 from sugarcane bagasse. However, extractives may be a great source of value in major-
29 scale biorefineries for cellulosic ethanol production from bagasse.⁹

30 **6 Biomass to bioethanol**

31

32 Efficient hydrolysis of the sugarcane bagasse along with the subsequent fermentation of
33 sugars creates a compelling commercial opportunity. According to Linoj *et al.*⁸¹
34 sugarcane encompasses two thirds of the production of sugar in the world. The
35 advantages of biorefining sugarcane bagasse to bioethanol would include an ease of
36 production when integrated into a sugarcane ethanol existing mill, hence lowering any
37 necessary investments.

38 **6.1 Sugarcane Bagasse to Bioethanol**

39 A study presented by Walter *et al.* showed that if 76% of bagasse is pretreated and
40 enzymatically hydrolyzed for sugar, this sugar could be fermented to yield up to 149.3

1 liters of ethanol per ton of bagasse.⁸² Other studies suggest that in a two step pretreatment
2 using a dilute acid pretreatment condition at 175°C for 40 min and 1% H₂SO₄
3 concentration with a 1:1 solid liquid ratio, followed by an organosolv treatment, it is
4 possible to achieve 192 liters of ethanol per ton of bagasse. Whereas using similar
5 conditions, 120°C for 40 min with 1% H₂SO₄ concentration with a 1:4 solid liquid ratio
6 followed by organosolv, ethanol generation could produce up to 180 liters of per ton of
7 sugarcane bagasse.⁸³ Different pretreatments and pathways for hydrolysis and
8 fermentation have varying effects on glucose concentration available for fermentation
9 contributing to different ethanol production (Table 9).

10 Cogeneration systems are very common in sugar mills.^{23, 84} When using cogeneration
11 systems for first and second generation production simultaneously in different boiler
12 pressures (2.2-9.0 MPa), it was shown that the system using 2.2 MPa achieved a
13 maximum yield of anhydrous ethanol production of 113.7 liters per ton of sugarcane.⁸⁵
14 According to Dias *et al.*⁸⁶ the double-effect distillation process of sugarcane bagasse is
15 compared to conventional distillation. In the double-effect process, the distillation
16 columns operates under vacuum pressures ranging from 19-25 kPa and the rectification
17 columns pressure ranges from 101-135 kPa with an extractive distillation process using
18 monoethyleneglycol (MEG) for ethanol dehydration, providing higher yields of
19 anhydrous ethanol from bagasse than conventional (Table 10). Hemicellulose pentoses,
20 mainly xylose and arabinose, are difficult to transform for the production of second-
21 generation bioethanol, hence metabolic microorganisms are necessary to succeed on
22 pentose.⁶⁶ Thus, pretreatment of bagasse is necessary in order to modify chemical
23 composition, size and structure in such manner in which hydrolysis can be carried out
24 promptly and with increased yields.

25 **7 Biomass to Biopower**

26 Power generation in the world is another cause of increased pollution and climate
27 changes. Countries are seeking renewable energy sources for electricity production for
28 the foreseeable future. In 2009, the Energy Information Administration (EIA) compared
29 renewable electricity to net generation (Table 11) of the top 5 countries. Although China
30 and United States are the leading net power generation countries, at 576.605 and 429.652
31 billion kWh respectively, currently, their renewable power energy profiles are less than
32 17% of the electricity generated. By contrast, Brazil and Canada have been more
33 successful regarding renewable energy, producing 89.6% and 63.3%, respectively of the
34 total energy produced from renewable sources, chiefly hydroelectric power.

35 Cogeneration systems generate electricity and thermal energy at high output capacities. In
36 2004 Cuba reached 600 MW of cogeneration capacity in the 85 sugarcane mills active.^{22,}
37 ²³ If 45 of the active 85 mills, which has a capacity of 4600-14000 ton of cane a day,
38 were modernized cogeneration capacity would increase substantially to 1400-1600
39 MW.²²

40 **7.1 Sugarcane Bagasse to Biopower**

41 Sugar and ethanol plants often utilize sugarcane bagasse as a source of fuel because it can

1 produce enough power and heat to meet all needs. These plants are self-sufficient in
2 energy consumption and often still have a surplus of bagasse which can present
3 environmental concerns due to its prolonged on site accumulation, which poses a threat
4 for higher spontaneous combustion possibility.⁸⁷ The mills in Brazil generate on average
5 12kWh of electricity per ton of sugarcane bagasse, 330 kWh of heat energy and 16kWh
6 of mechanical energy.⁸⁴

7 Steam-based sugarcane mills can be found in countries like Cuba and Brazil, which
8 utilizes two types of steam turbines for low pressure steam and electricity production:
9 Condensing Extraction Steam Turbine (CEST) and Backpressure Steam Turbine
10 (BPST).^{23, 88} CEST are high-pressure turbines used in sugar factories that are favored for
11 pressure levels above 65 bar.⁸⁹ Any accessible residue from sugarcane processes such as
12 lignocellulosic biofuel would be implemented for generating electricity. BPST, on the
13 other hand, are non-condensing turbines, commonly found in refineries, in which exhaust
14 steam at lower pressure loads and are usually cheaper than condensing turbines. BPST
15 could generate up to 99.51 kWh per ton cane and fulfill electricity demand at the mills,
16 while CEST could generate 121 kWh per ton cane, meet the energy demand at the mills
17 and would export the surplus electricity, approximately 93 KWh per ton cane for public
18 use (Table 12).⁸⁸ Alves *et al.*⁸⁸ also revealed that CEST yielded a surplus of electricity,
19 unlike BPST because all available bagasse is consumed as fuel.

20 Gasification and Fischer-Tropsch (GFT) conversion process for sugarcane bagasse has
21 been studied and concluded to be effective in energy efficiency for both liquid fuel
22 production and overall energy when compared to other conversion process such as acid
23 or enzymatic hydrolysis and saccharification and fermentation processes.^{82, 83} Research
24 studies by of Walter *et al.*⁸² using sugarcane residues, trash and bagasse were analyzed
25 for production of ethanol and electricity in terms of hydrolysis and gasification and
26 Fischer-Tropsch processes. Multiple variables to avoid emissions of greenhouse gas
27 emissions were hypothesized and it was concluded that GFT was slightly more feasible
28 and effective where the estimated avoided emissions was 263.9 kg CO₂ equivalents per
29 ton of carbon, with 67% from conventional ethanol production and 11% from surplus
30 electricity production. While the same variables were taken into consideration in the
31 hydrolysis process, the avoided emission was estimated to be 253.2 kg CO₂ equivalents
32 per ton of carbon, with 94% from ethanol production and 6% from surplus electricity
33 production. Another study determined that the avoided carbon dioxide emissions were
34 larger for maximum ethanol production than that of the electricity production, concluding
35 that a plant in which produces ethanol is more desirable then a plant that produces
36 electricity using bagasse in order to avoid CO₂ emissions.⁹⁰ These processes are still
37 under development and it is unknown which method is superior or more feasible and cost
38 effective for a commercial scale.

39 **8 Conclusions**

40 Sugarcane is one of the most abundant crops in the world having innumEROUS mills and
41 plants for sugar extraction and first generation ethanol production. Most Latin American
42 countries possess tropical climates enabling them to generate sugarcane crops. Brazil
43 alone is the greatest sugarcane producer utilizing ethanol for majority of its cars sold

1 followed by Mexico and Colombia, and other countries with great potential for both
2 bioethanol and biopower growth. Bagasse is a promising agricultural residue in the
3 bioethanol production and power generation due its high cellulose and average lignin and
4 hemicellulose content.

5 Pretreatment is one of the most crucial steps for ethanol production. Although there is not
6 a specific pretreatment that is most used for commercial purposes and is cost-effective,
7 the appropriate method of pretreatment followed by acid or enzymatic hydrolysis and
8 fermentation is important for high yields in the conversion of sugars to ethanol.

9 Commonly used are steam explosion, which is used for alteration of cellulose
10 crystallinity and degree of polymerization, and dilute acid, which transforms a solubilized
11 portion of hemicellulose into fermentable sugars. Similarly in power generation, specific
12 processes have not been utilized in a commercial scope, CEST turbines and GFT
13 conversion method appears to be promising due to its higher surplus electricity and hence
14 energy efficiency.

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41 Table 1 Sugarcane production

Sugarcane crops	Brazil ¹	Mexico ^{21, 91}	Colombia ¹⁷	Argentina ^{16, 92}	Cuba ²² , ^{23, 93}	India ²⁵	Thailand ¹⁵	China ¹⁵	World ^{15, 17}
Year	2013	2012	2013	2010	2009	2012-2013	2013	2013	2013

Average production (million metric ton yr^{-1})	743	42.5-44.6	21.5	19	11.6	341.2-350	100.1	125.5	1877.1-1911
Average annual yield of sugarcane (metric ton ha^{-1})	120	65	108	56	22.4	70	62.6		-

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2 Table 2 Characteristics of major sugarcane species

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Reference: ^{6, 55, 94}	<i>S. officinarum</i>	<i>S. spontaneum</i>	<i>S. robustum</i>	<i>S. sinense</i>	<i>S. barbieri</i>	<i>S. edule</i>
Culms thickness (cm)	3.5-6	~4	2.0-4.4	~2	~2	-
Height of plant (m)	1-6	5	10	5	5	-
Chromosome number	2n=80	2n=40-128	2n=60-~200	2n=80-124	2=111-120	2n=60-80
Classification	Noble canes	Wild species	Wild species	Ancient hybrid	Ancient hybrid	Wild species

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3 Table 3 Different pretreatment conditions for sugarcane bagasse

Pretreatment	Operating Conditions	Reference
Steam explosion	0.6-4.8MPa, 160-260°C, 15 min	^{33, 95}
Hot water	120-230 °C, 1-80 min	^{37-39, 83}
Alkaline	53.2-120 °C, 4-65.6 h	^{33, 46}
Organosolv	150-200°C, 30-90 min, 35-70% of solvent	^{33, 37, 45, 83}
Dilute acid	100- 120 °C, 40-120 min, 1.8%-10% of acid concentration	^{42, 96}
Concentrated acid	80 °C, 90 min, 18%-40% of acid concentration	⁴²
Ionic Liquids	60-140 °C, 5-360 min, 3-10% of solvent	^{48, 50-52}
Dilute acid (1) + microwave heat (2)	(1) 1.56 % of acid concentration, 0.2M, pH 0.68 (2) 130-190 °C, 5-10 min, 2.45GHz, 900W	⁴¹

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3 Table 4 Degree of polymerization of isolated cellulose of sugarcane bagasse and
 4 crystallinity index of commercial type bagasse

Cellulose of sugarcane bagasse					
	Cellulose A ^{a,56}	Cellulose B ^{b,40}	Cellulose C ⁹⁷	Cellulose D ⁹⁸	Cellulose E ⁹⁹
DP _w	822.5-1406.5	1858.1-2040.8	1277.0	1309.6	1356.0
Intrinsic Viscosity (η , ml g ⁻¹)	256.3-415.6	534.1-631.6	378.0	387.2	399.5 ^c
Molecular Weight (M _w , g mol ⁻¹)	133250-227850	301000-362600	206800	212150	Not reported
Sugarcane bagasse commercial variety					
	SP79-1011 ⁵⁷	RB867515 ⁵⁷	SP81-325 ⁵⁷	RB92579 ⁵⁷	Bagasse E ⁹⁹
CrI %	52.7	55.8	52.6	60.4	62.0

^{a,b} range of 6 isolated cellulose of bagasse under different isolation conditions
^{c,56} intrinsic viscosity (η) calculated from $DP_w^{0.9}=1.65(\eta)$

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2 Table 5 Content of neutral sugars and uronic acids of isolated hemicellulose from sugarcane
 3 bagasse

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Isolation of Hemicellulose	Xylose (%)	Arabinose (%)	Glucose (%)	Galactose (%)	Mannose (%)	Rhamnose (%)	Uronic Acids (%)
Dewaxed + distilled water ⁵⁹	55.20	10.73	20.42	7.68	4.13	1.84	6.95
NaOH ⁵⁹	81.37	11.93	3.97	1.78	0.47	0.48	3.50
NaOH + H ₂ O ₂ ⁵⁹	85.02	8.65	5.87	0.46	Trace	Not detectable	1.75
H ₂ O ^{a, 61}	57.43	6.25	28.52	6.36	-	-	1.44
H ₂ O + KOH ^{a, 61}	79.92	5.5	12.03	0.88	-	-	1.67
KOH ^{b, 68}	83.1-84.6	11.0-12.1	2.1-3.1	0.5-0.7	-	-	1.4-2.6
H ₂ O ₂ ^{c, 67}	73.1-82.6	3.8-7.2	3.8-7.9	-	-	-	3.6-7.0

^a precooked with H₂O₂ and MgO

^b range composition of 7 isolated hemicellulose

^c range composition of 19 isolated hemicellulose

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3 Table 6 Lignin content in sugarcane bagasse from different variety of sugarcane

Sugarcane variety	Lignin content in sugarcane bagasse (%)		
	Klason lignin	Acid-soluble lignin	Total lignin ^a
Hybrid 140 ¹⁰⁰	-	-	21.5 \pm 0.2
Hybrid 321 ¹⁰⁰	-	-	20.2 \pm 0.4
Hybrid 58 ¹⁰⁰	-	-	18.6 \pm 0.1
Hybrid 146 ¹⁰⁰	-	-	18.6 \pm 0.1
Hybrid 89 ¹⁰⁰	-	-	16.8 \pm 0.1
PE-BR ^{b,101}	-	-	21.1 \pm 0.9
NA-BR ^{c,9}	19.7 \pm 0.1	2.2 \pm 0.2	21.9 \pm 0.3
Raw bagasse ⁶⁹	25.9 \pm 0.3	4.7 \pm 0.3	30.6 \pm 0.6
Raw bagasse B ¹⁰²	22.9 \pm 0.7	0.06 \pm 0.0	23.0 \pm 0.7
RB867515 ⁷²	17.8 \pm 0.6	2.2 \pm 0.2	20.0 \pm 0.8

^a sum of klason and acid-soluble lignin
^b sugarcane bagasse from Pernambuco - Brazil
^c sugarcane bagasse from Nova America - Brazil

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3Table 7 S:G:H ratio of lignin in sugarcane bagasse

	Ball milled lignin ⁶⁹	Ethanol lignin ⁶⁹	Water soluble lignin ⁶⁹	Dioxane lignin ⁶⁹	Ball milled 2 lignin ⁷²	Whole cell wall lignin ⁷²
Lignin aromatic units						
S (%)	55.4	58.4	53.6	55.0	60.0	60.0
G (%)	39.1	30.5	32.5	38.3	38.0	37.0
H (%)	5.5	11.1	13.9	6.7	3.0	2.0
S/G ratio	1.4	1.9	1.6	1.4	1.6	1.6
<i>p</i> -coumarate/ferulate ratio	9.8	4.5	1.9	6.2	2.6	12.0

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4 Table 8 Chemical characteristics of sugarcane bagasse ash

(%)	Bagasse ash 1 ⁷⁷	Bagasse ash 2 ¹⁰³	Bagasse ash 3 ⁷⁶	Bagasse ash 4 ⁷⁸
SiO ₂	61.59	72.95	85.55	80.2
Al ₂ O ₃	5.92	1.68	2.29	2.60
Fe ₂ O ₃	7.36	1.89	1.21	5.60
K ₂ O	6.22	9.28	1.33	4.00
CaO	5.00	7.77	4.05	1.80
MnO	0.10	-	0.08	0.20
TiO ₂	1.46	-	0.20	1.40
SO ₃	0.42	4.45	2.28	0.10
MgO	1.17	1.98	-	1.60
P ₂ O ₅	0.98	-	3.01	1.40

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6 Table 9 Ethanol yield from fermentation of SHF and SSF under different pretreatments

	Parameters		
Bagasse pretreatment	Initial glucose concentration (g L ⁻¹)	Ethanol produced (g L ⁻¹)	Ethanol yield (% ethanol produced by gram of glucose)
Separate hydrolysis and fermentation (SHF)			
SEB ^{a,102}	57.7 ± 1.4	25.6 ± 0.3	44.4
SA-AWB6 ^{b,102}	50.1 ± 0.2	23.4 ± 0.2	46.6
SA-AWSEB ^{c,102}	50.1 ± 1.4	20.4 ± 0.1	40.8
AH ^{d,9}	57.8	25.2	43.6
H ₃ PO ₄ ⁹	54.9	24.9	45.4
H ₂ SO ₄ ⁹	54.9	20.1	43.7
Simultaneous saccharification and fermentation (SSF)			
AH ^{d,9}	54.9	18.8	34.2
H ₃ PO ₄ ⁹	53.4	16.9	31.6
H ₂ SO ₄ ⁹	48.2	18.4	37.2

^a Steam-exploded bagasse^b Sono-assisted alkali-washed bagasse^c Sono-assisted alkali-washed steam-exploded bagasse^d Autohydrolysis (Liquid hot water) bagasse

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4 Table 10 Sugarcane juice and bagasse results from conventional and double-effect
5 distillation processes

Reference: ⁸⁶	Conventional distillation	Double-effect distillation
Anhydrous ethanol from bagasse (L t ⁻¹ cane)	18.8	22.0
Anhydrous ethanol from sugarcane juice (L t ⁻¹ cane)	83.7	83.7

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4 Table 11 Top 5 countries in electricity generation and its renewable use

Reference: ¹	Generated electricity (billion kWh)	Renewable electricity %
China	576.605	16.7
USA	429.652	10.9
Brazil	410.258	89.6
Canada	371.008	63.3
Russia	165.227	17.8
World	3760.590	-

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5 Table 12 Electricity productions in BPST and CEST system

System	BPST		CEST			
Condition of turbine	1.9MPa, 593K (7MW) ²³	2.2- 10MPa, 573- 803K ⁸⁸	6.0MPa, 754K ¹⁰⁴	4.2MPa, 693K (38MW) ²³	6.3MPa, 793K (30MW) ²³	6.5-10MPa, 753-803K ⁸⁸
Electricity generated (KWh t ⁻¹ cane bagasse)	22.79	38.62- 99.51	114.00	110.00	130.00	105.48- 121.22
Electricity surplus (KWh t ⁻¹ cane bagasse)	-	10.62- 71.51	90.20	85.00	105.00	77.48-93.22

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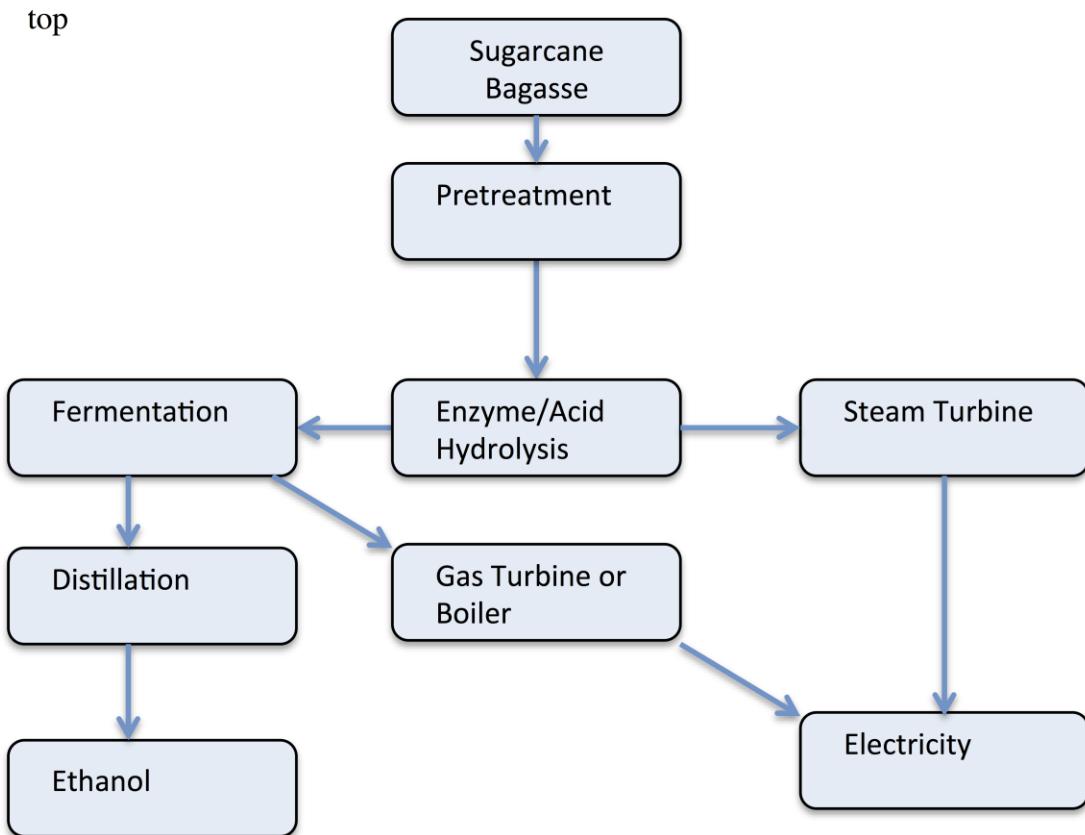
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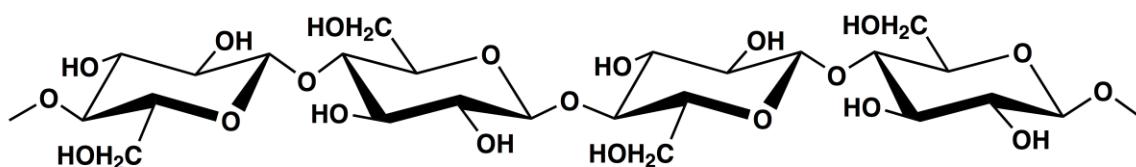
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Tais L Bezerra Figure 1 Bioethanol and Biopower process from second-generation biomass

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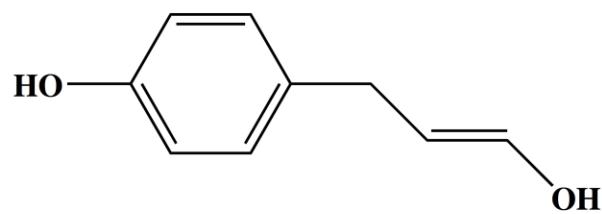
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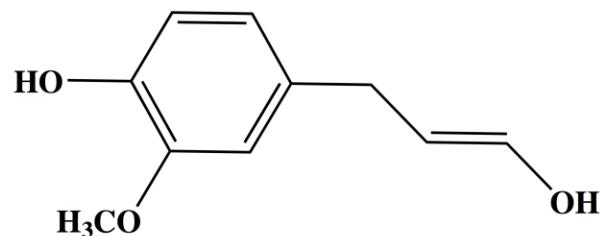
Tais L Bezerra Figure 2 Structure of Cellulose

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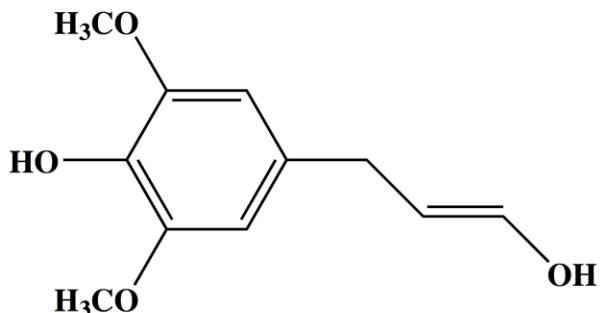
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Tais L Bezerra Figure 3 Lignin structure with a) p-coumaryl alcohol
b) Coniferyl alcohol and c) Sinapyl alcohol

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