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NEW BUSINESS OPPORTUNITIES IN THE SUGAR-ALCOHOL INDUSTRY:

ALCOHOL CHEMISTRY AND BIOREFINERIES

Telma Teixeira Franco and *Camilo López Garzón*

BIOREFINERIES: DESCRIPTION AND PRINCIPLES

Biorefinery is an integrated process in which biomass is converted to higher added value products with zero or near zero net CO_2 emissions. The biorefinery concept is based on the similar concept behind traditional petrochemical refineries and partially uses related transformation processes. However, the main value-adding technologies associated with biorefineries are more complex, offering a greatest potential given the huge variety and quantity of renewable biomass and derived products. In addition, the biorefinery provides the possibility to develop non-polluting and sustainable industries with low environmental impact.

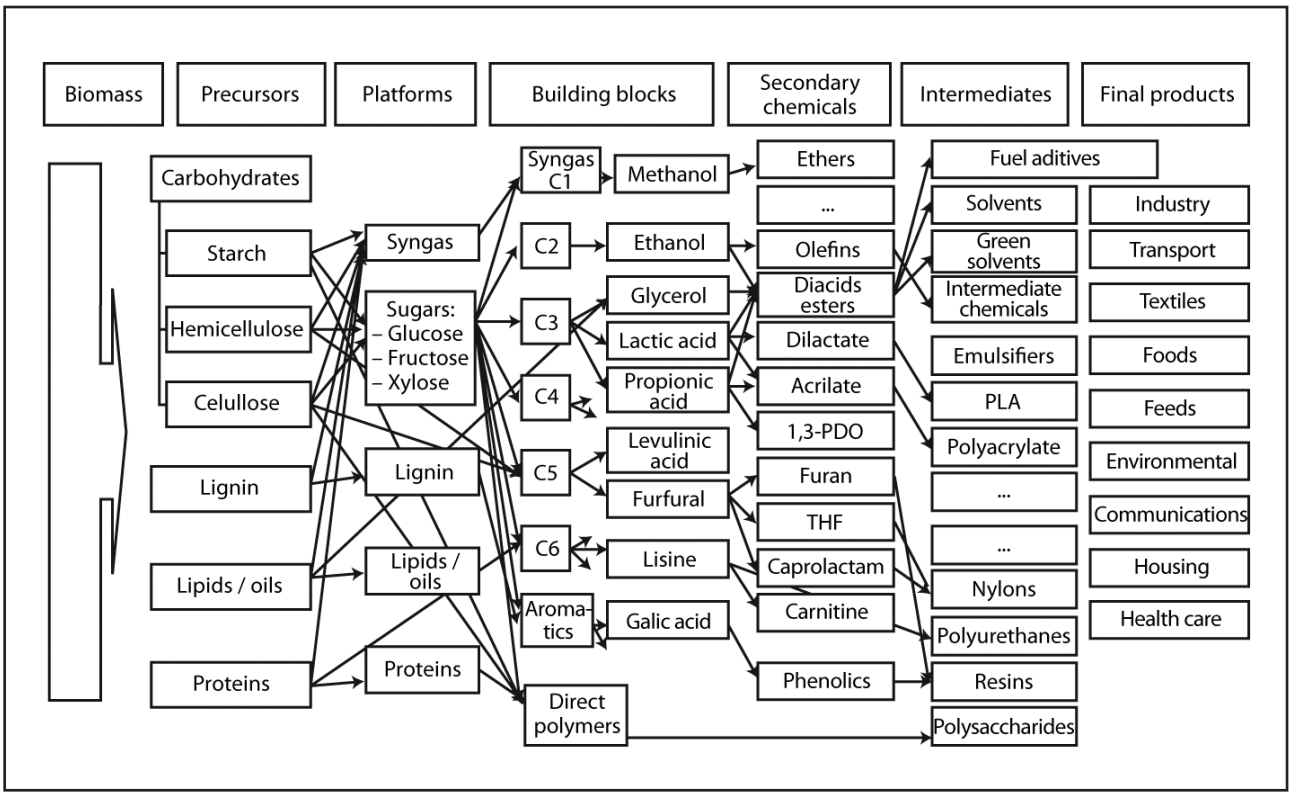
Historically, it is known that several processes, today included in the area of biorefinery, were already known since the 19th century, such as the saccharification of wood, solubilization of cellulose, sugar refinery, starch and maltodextrins for industrial purposes, vegetal oil and chlorophyll extraction, furfural production from bran distillation, isolation of vanillin from lignin (already developed in 1874) and lactic acid production by fermentation (KAMM *et al.*, 2006).

Different types of biomass are currently being used for the production of molecules for subsequent use in industrial processes, which can lead to gradual replacement of the petrochemical platform. Among them, building blocks had gained big interest; these are molecules with multiple functional groups, which can be converted into other molecular groups (Figure 1).

In order to obtain chemical building blocks, basically two essential biomass processes need to be developed: a) hydrolysis of polysaccharides originated from lignocellulosic materials with sugar releasing and b) fermentation of this sugars to products of interest. Enzymatic or chemical reactions may be part of the step sequence to obtain the building blocks. Thus, the above mentioned processes must be into a biorefinery facility and lead to several conceptual definitions. Various concepts of biorefinery are associated to ideas about how the biomass should be sustainably converted into chemicals, materials, fuels and energy, satisfying the current economic constraints (KAMM *et al.*, 2006). Another concept of biorefinery is directed to maximize the economic value of biomass, improving business and industrial models (STUART, 2006) (Figure 2).

Different technologies need to be integrated in order to achieve widespread and efficient potential of biorefinery, as metabolic design of biochemical pathways (i.e. metabolic engineering), use of raw material (biomass knowledge) and production of chemical intermediates and final products (industrial processes) (Figure 3).

Biorefineries using biochemical routes, should be able to operate based on biomass precursors (mainly carbohydrates in the case of lignocellulose); obtain those requires a number of separation/fractionation steps, usually by means of physical transformation processes. Once the fractions of biomass are obtained they can be chemical and/or microbiologically processed and fed to conventional industries. This approach was described



Source: Based on KAMM *et al.,* 2006.

FIGURE 1 Biomass-based platform.

(KAMM B. and KAMM M., 2004) and summarized by the following expression:

Raw material (non fractionated) + Combination of processes → Miscellaneous products

Therefore, in order achieve an integrated production of food, animal feed, chemicals, materials and fuels an important key concept is to develop and establish the above described industrial com-

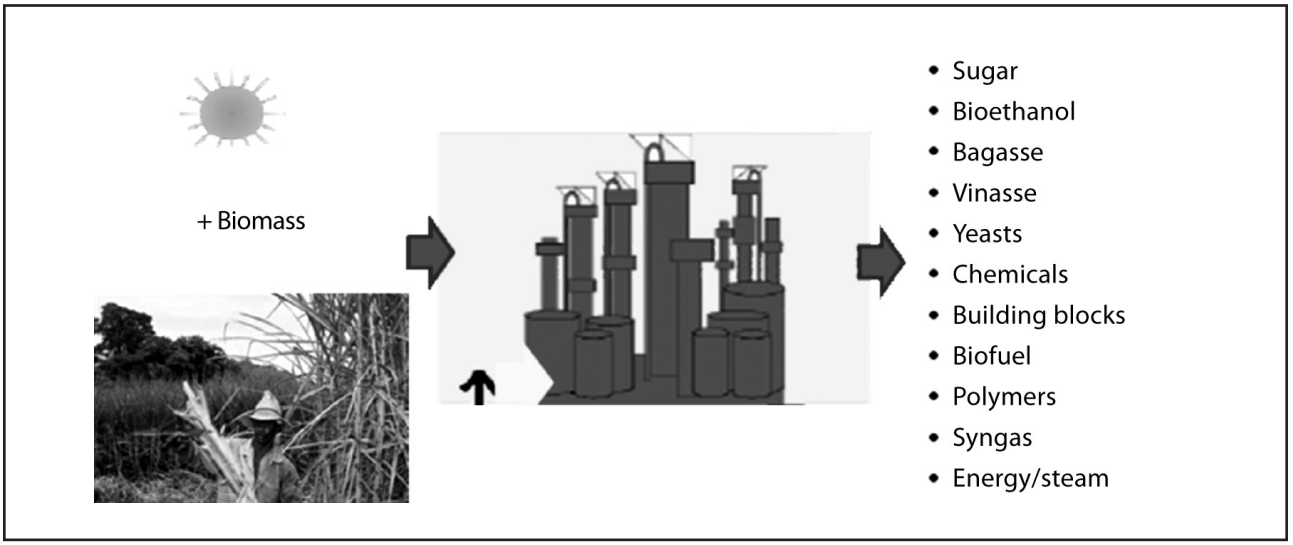


FIGURE 2 Schematic of sugarcane refinery.

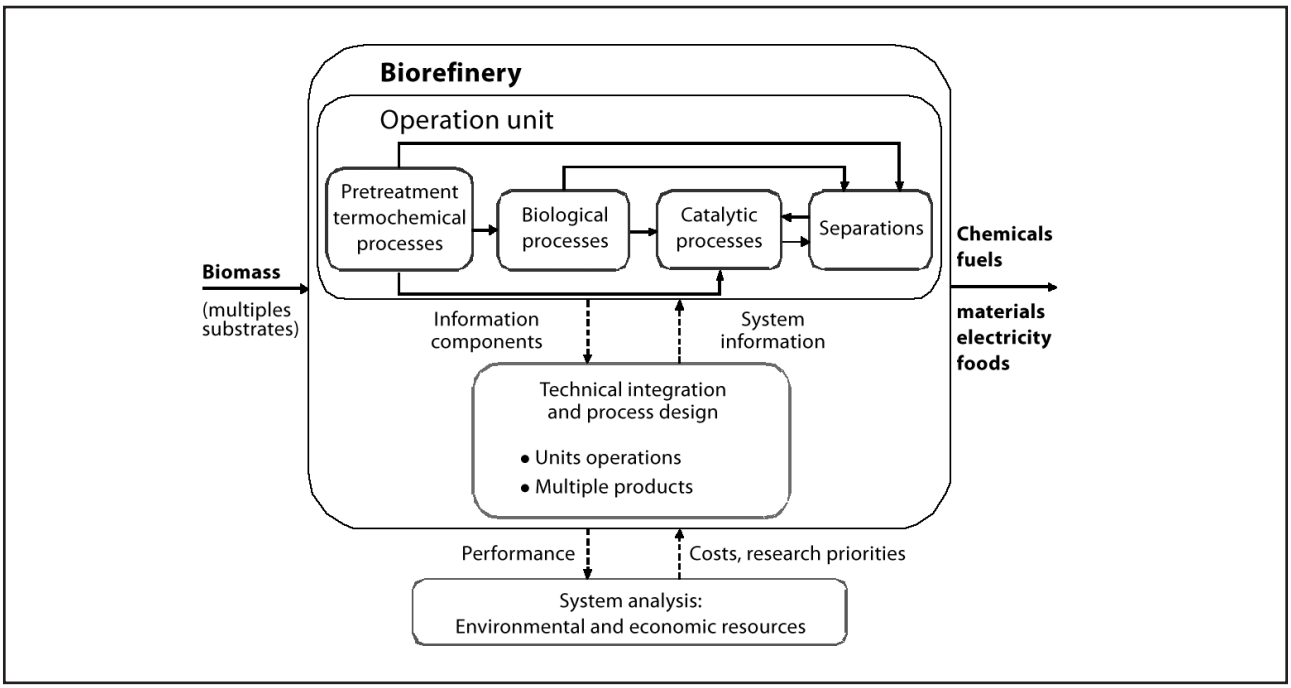


FIGURE 3 Schematic of biorefinery concept.

plex facilities instead of individual isolated ones (U.S. NRC, 2000).

THE FULL EXPLOITATION OF BIOMASS

The strong global economic growth has accelerated the demand for sustainable resources used in industrial production; energy resources may originate from different sources such as wind, water, biomass, nuclear fission and fusion, however material resources mainly depend on biomass in particular vegetal biomass. In 2001 it was estimated that only $6x10^9$ tons/year of biomass were used within $170x10^9$ T/year produced by nature, and only 3% are used for industrial purposes (ZOEBELIN, 2001). Current literature report that between 9% to 13% of biomass is already used in some regions for energy purposes (KRAUSMANN *et al.*, 2008). These resources can be more efficiently used; nevertheless, the increased efficiency is hampered by the inherent characteristics of the vegetal biomass. The separation (fractionation) of biomass into its major components for subsequent processing is a major obstacle to the establishment of biorefineries. One of the research priorities outlined by the U.S. National Research Council (U.S. NRC, 2000) is the development of efficient procedures for processing lignocellulosic materials in order to obtain materials susceptible of transformation by means of biotechnological and/or traditional chemistry. In the case of biomass from sugarcane, efficient processes of pretreatment, aimed on separating the cellulose from hemicellulose and lignin, and the different types of hydrolysis (acid, enzyme or combined) will soon be available on an industrial scale, ensuring the almost complete utilization of biomass.

As soon as the processes for biomass depolymerization have been established, the main precursors available as raw materials in the bio-based sugarcane industry are the two most abundant simple carbohydrates in nature, glucose and xylose (LYND *et al.*, 1999; PANDEY *et al.*, 2000). A new bioproduct platform based on these precursors should be developed.

THE RAW MATERIAL AS DRIVING FORCE IN THE DEFINITION OF TECHNOLOGIES

Since the end of the last decade, has been recognized that the greatest impediment for a global application in large-scale of the biorefinery

concept is the lack of low-cost biomass processing technologies (LYND *et al*., 1999). According to HAHN-HAGERDAL and colleagues (2008), the efficiency and cost of technologies currently used to produce sugar syrup with good fermentation quality could be improved, despite recent progress. The cost distribution of these processes depends on the type of raw material, availability and even more of their required pretreatment.

For a long time has been an objective the development of microorganisms with the ability to convert the biomass components in various products with associated good yields at high final concentrations, thus trying to improve the economy of bioprocesses. Two routes have appeared naturally, the first one focused on improve the selectivity of native microorganisms capable of use given substrates (product-centered development). The latest one aims the inclusion of certain substrate consumption features in microorganisms with good production capacity of target compounds (substrate-centered development) (LYND *et al*., 1989). The first route is currently being used to obtain high-value bioproducts, where the raw material costs has little impact on the overall production cost.

In the case of commodities production in biorefineries, processes and biocatalysts involved should be designed based on the characteristics of biomass (substrate) used as feedstock, and should make the best use of it in each step. Thus, the development to be achieved depends on the type of biomass available for processing. Hence, the biorefineries have been classified according to the biomass used; the most frequently cited classification refers to lignocellulosic (considered the most important given the abundance of lignocellulosic feedstocks), grains and grass-based biorefineries (KAMM B., KAMM M., 2004).

Another classification has arisen for the biorefineries destined to fuel production; such classification denotes a technological differentiation among them ranked by *generations*: those based on precursors commonly used as food (vegetable oil, sugar and starch) can be typified as first generation biorefineries. Second generation facilities uses biomass feedstock not commonly regarded for food purposes. Recent studies show that the use of biomass not dedicated to food purposes, i.e. from trees (wood and their subproducts), grass and lignocellulosic materials will be greatly improved since the transformation processes hold better energy balance in comparison with the first generation (TAYLOR, 2008).

THE LIGNOCELLULOSIC BIOREFINERY: ALTERNATIVE TO THE SECTOR

In an industry where the main byproducts, bagasse and straw, are lignocellulosic materials it is straightforward the establishment of a biorefinery based on this biomass. The lignocellulosic material is composed of three precursors, lignin (a phenolic polymer or macromolecule according to some authors), hemicellulose (polymer composed of pentose, mainly xylose) and cellulose (glucose polymer). According to KAMM and KAMM (2004) these three precursors are transformed using the equations:

$$\text{Lignocellulose} + H_2O \rightarrow \text{Lignin} + \text{Cellulose} + \text{Hemicellulose} \quad (1)$$

$$\text{Hemicellulose} + H_2O \rightarrow \text{Xylose} \quad (2)$$

$$\text{Xylose } (C_5H_{10}O_5) \xrightarrow{\text{catalist}} \text{Furfural } (C_5H_4O_2) + 3H_2O \quad (3)$$

$$\text{Cellulose } (-C_6H_{10}O_5-) + H_2O \rightarrow \text{Glucose } (C_6H_{12}O_6) \quad (4)$$

Equation 1 represents the fractionation of these three polymers, but not exactly the hydrolysis, nevertheless the separation of these fractions is still only achieved by wet pretreatment.

The process lines of the above mentioned precursors are shown in Figure 4.

A huge amount of microbial conversions based on glucose can be used in these biorefineries; those have been studied since the beginning of the industrial microbiology, are very well documented and, in general, favorable energetically. Therefore the line of production from glucose has the most potential, being ethanol the main product currently. This alcohol can be chemically transformed into ethylene, which could be supplied directly to petrochemical refineries in order to produce polyethylene and polivinilacetate. Other well-known products from glucose are hydrogen, methane, propanol, acetone, butanol, butanediol, succinic and itaconic acid (ZEIKUS *et al*., 1999).

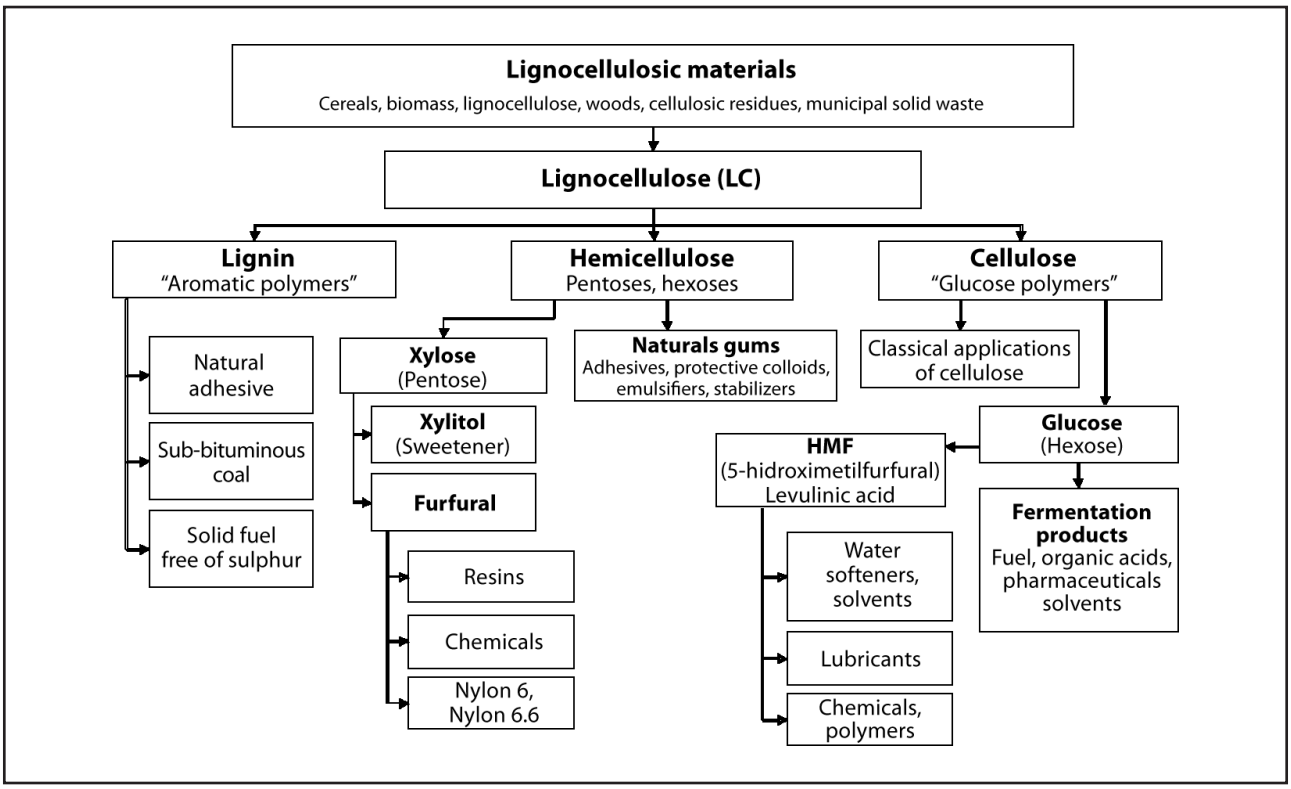


FIGURE 4 Biorefinery based on lignocellulosic residues from straw and sugarcane.

In the case of the production line based on xylose as precursor, was found a shortage of processes developed intending using this feedstock in the generation of bioproducts. Cases such as production of xylitol (sweetener), offers only a marginal advantage of this abundant source of carbon. Recently processes are being developed having as main goal the production of ethanol from xylose using recombinant microorganisms, since there are barriers on the xylose metabolism towards ethanol (JEFFRIES, 2006), these processes so far have been unsuccessful. A product with exciting potential is furfural, which can be used in the production of nylon, returning then to the original process established long time ago, but not in production nowadays. In summary new alternatives for the utilization of xylose should be developed.

Regarding to the lignin as precursor, there are many issues to be solved, the potential is well understood considering the nature of compounds that could be produced, like mono-aromatic hydrocarbons which high value on the market. However, the recovery of those bioproducts is difficult and their applications are limited.

THE NEW BIOCOMMODITIES PLATFORM

In 2004 was published a joint study between the Pacific Northwest National Laboratory U.S. – PNNL and the National Renewable Energy Laboratory – NREL a selected list of chemicals potentially obtained from biomass that would be essential for the gradual replacement of the petrochemical platform (WERP and PETERSEN, 2004). Since it was recognized these compounds could lead to a partial replacement of the known chemical platform, was assigned to those the name of *building blocks*, whereas their multiple functional groups could then be used to obtain other compounds. This preliminary study suggested initially 300 molecules having the characteristics of building blocks, this first selection was quickly reduced to 30 and then to a final 12, which can be produced from sugars and subsequently converted to materials and high

– value chemicals. At the end of the study, the list of building blocks consisted of: 1,4-dicarboxylic acids (succinic, fumaric, malic), 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol.

The current literature describes the planning and construction of some production plants for the development of industries based on renewable resources, such as the production of 1,3-propanediol (DUPONT, USA), polylactic acid (CARGILL, USA), PHB (by the Metabolix consortium formed by ADM from USA and PHB from Brazil), amino acids (Ajinomoto), succinic acid (DSM) and polyethylene (pilot plant in Triunfo, RS; industrial plant under construction by Braskem from Brazil). The production of polypropylene has also been announced by the brazilian Braskem, in addition Amyris-Votorantim, in partnership with Cristalsev and Santaelisa Vale had installed a pilot plant in Sertãosinho (State of São Paulo) for a diesel-like fuel production from sugarcane sucrose, using genetically engineered yeast of the genre *Saccharomyces*.

SUGARCANE BAGASSE AS RAW MATERIAL IN BIOREFINERIES

One of the biggest byproducts of the ethanol industry is the sugarcane bagasse, a cellulosic residue obtained after extracting the sugarcane juice. Currently the bagasse is used as a primary source of energy in most Brazilian mills and as raw material in paper production in some countries (PANDEY *et al.*, 2000). Recently was identified the need of utilize better and more efficiently this material and use it as a source for precursors in the lignocellulosic biorefinery.

The bagasse from sugarcane is the fraction of biomass left after the cleaning procedures, preparation and extraction of the juice (by grinding or using diffusers), it is a heterogeneous biomass that varies in its composition as well as in their morphological structure depending on the procedures for cutting and processing (ROSSEL, 2006).

The production of bagasse is inherent to this industry, it is produced at high rates in Brazil, has a relative low cost (between US$ 30 to 40/T) (SATYANARAYANA *et al.*, 2007) and a composition full of precursors (Table 1).

The usage of sugarcane bagasse has been the main topic in many brazilian studies, used in the form of hydrolyzed in various biotechnological routes for production of ethanol, xylitol, microbial protein, flavorings and enzymes (cellulases, xylanases and ligninases) among others (PANDEY *et al.*, 2000) and even as a biomaterial for the immobilization of cells (SANTOS *et al.*, 2008).

ETHANOL AND ALCOHOL CHEMISTRY

In Brazil, the biobased platform intended to replace the petrochemical technology is pioneer, being one of the world countries leading the production of ethanol, despite this other bioproducts are still in a very early stage of development. Since Brazil is technologically advanced in the produc-

TABLE 1 Typical composition of Brazilian sugarcane bagasse.

Fraction	% (dry base)
Cellulose	32-48
Hemicellulose	27-32
Lignin	19-24
Silica	0.7-3.5
Ash	1.5-5

Source: FINGUERUT, 2006.

TABLE 2 Estimated replacement for the U.S. aromatic derivatives.

Aromatic derivative	Current production (109 lb)	Required lignin (109 lb)
Benzene	20.4	90.7*
Toluene	11.1	
Xylene	13.8	
Terephthalic acid	11.1	12.7
Phenol	5.1	9.8
Total	61.5	113

* In order to substitute the requirements of benzene, toluene and xylene. Values in USA.

tion of ethanol, an alcohol chemistry derived platform can be installed in the country without major disruptions due to the easy access to raw materials, mostly in São Paulo state (Figure 5).

The products generated from ethanol are based on well-established ethanol chemistry, inherited from current refineries, processes like reforming, catalytic cracking and hydrocraking can be used to produce syngas that used in Fischer-Tropsch process or other catalytic process can generate a complete platform of derivatives. Recently there have been studies done in Brazil concerning the synthesis of heterogeneous catalysts using ethylene from ethanol and ethylene oxide, thereby producing a complete range of products such as plastic – PET, solvents, resins, paints, automotive fluids and other (MARTINS and CARDOSO, 2005).

THE THREE LINES OF BUSINESS IN BRAZIL

Lignin derivatives

The lignin (Figure 6) is a complex chemical compound that is an integral part of lignocellulosic materials, is a heterogeneous polymer with the structural function of maintain together chains of cellulose and hemicellulose.

The extensive use of lignin as a chemical precursor is still far from being achieved mainly due to the difficulties on their isolation. There are two problems to be solved in the recovery processes: maintaining the natural structure of lignin and get it at high yields. The processes developed to the date change in some degree the structure of lignin limiting their processing. Different methodologies for lignin isolation were developed, but in general, make extensive use of chemicals (which can react and degrade the lignin) hampering the desired recovery and quality.

Due to its aromatic characteristics, the lignin has been studied as a source of phenolic derivatives. In the United States projections about the total replacement of the phenolic derivatives for lignin derivatives were made (BOZELLI, 2004). These estimates showed that this substitution is feasible because all the chemical processes involved are in the actual state of the art; however the separation and purification of lignin remains

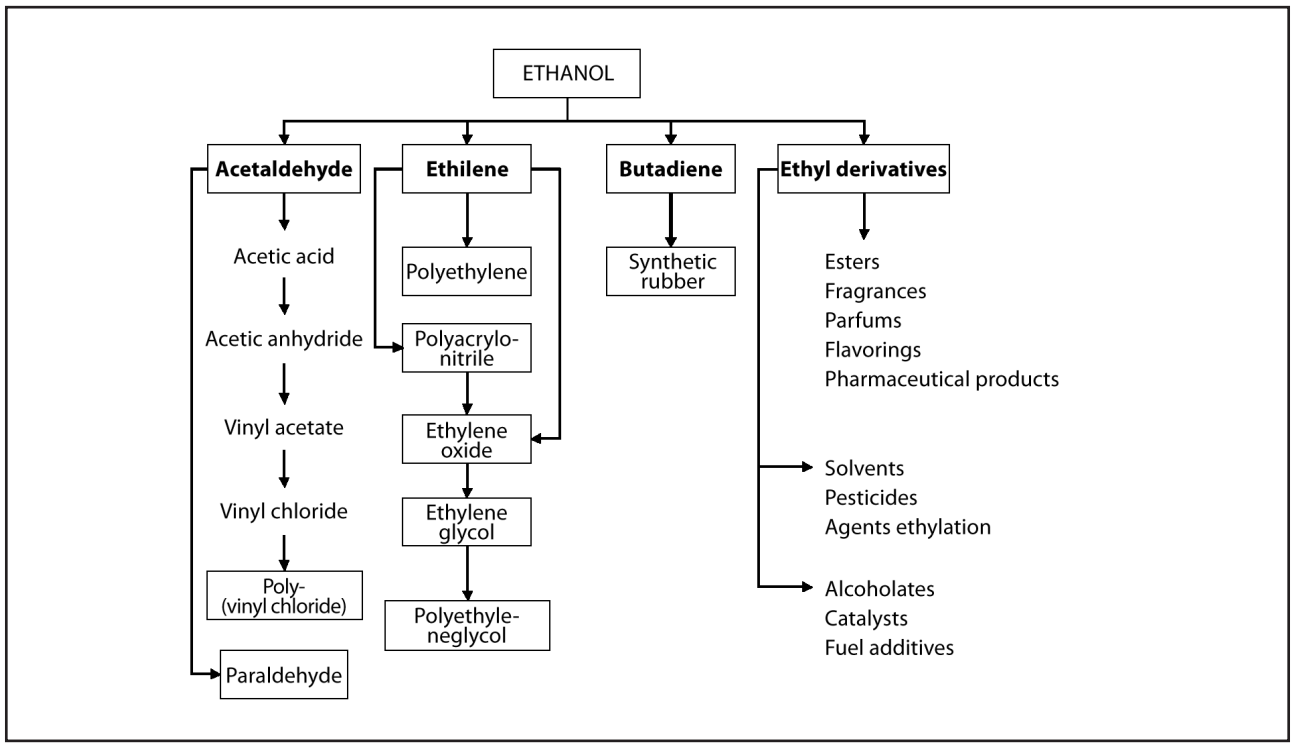


FIGURE 5 Platform chemical derived ethanol.

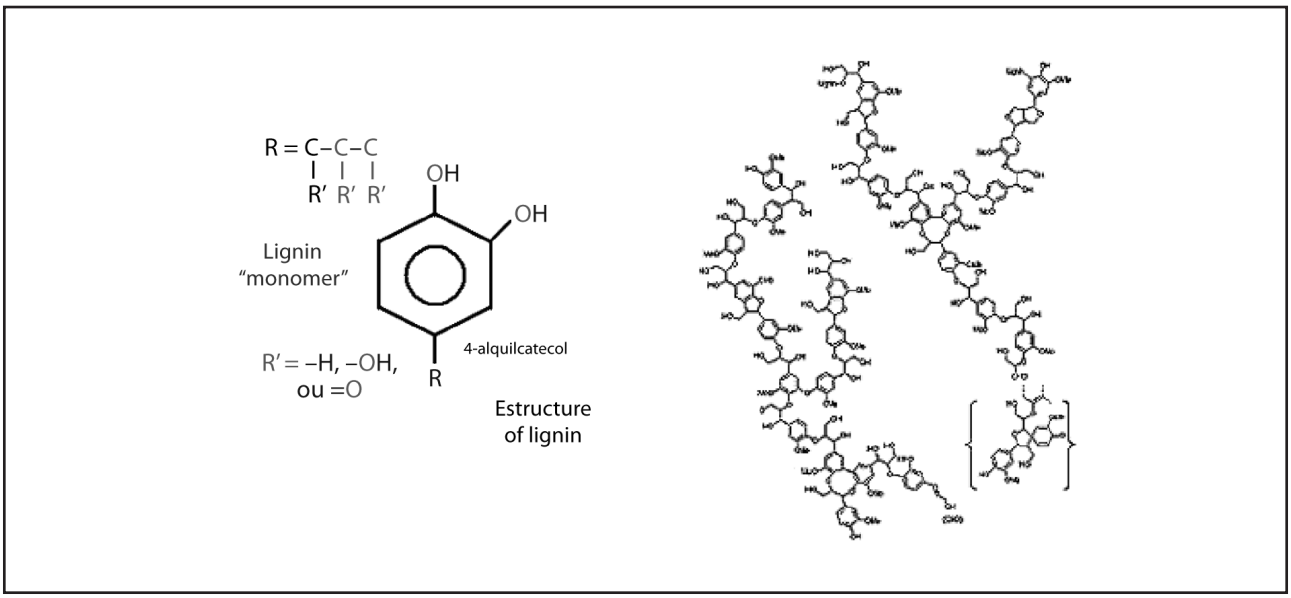


FIGURE 6 Structure of lignin.

as the main difficulties to overcome in order to achieve this goal.

The utilization of lignin can be classified into four groups according to the form of use: polymeric, monomeric or oligomeric (KAMM *et al.*, 2006):

- Polymeric form: as an adhesive for wood, cement additives etc.
- Oligomeric form: as co-reagent in the synthesis of polymers and resins.
- Molecules of low molecular weight monomers: mainly for the synthesis of vanillin and dimethyl sulfoxide.
- Fully degraded to gas, oil or coal via pyrolysis.

The use of lignin has been developed in Brazil in 2007 (mainly IN the monomeric form) to obtain catalytic oxidation products (aldehydes) as vanillin, syringaldehyde and p-hydroxybenzaldehyde, using as a source of lignin a product fraction from DFH – Dedini Fast Hydrolysis process. Certainly these products can add value to the process of separation and hydrolysis of sugarcane bagasse (SALES, 2007).

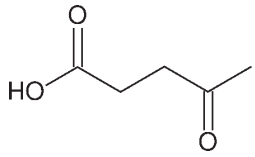
Utilization of cellulose (glucose)

Information about some of the building blocks not so well known in the country, suggested by the study of NREL and obtained from glucose are described below.

Levulinic acid – AL

The levulinic acid (Figure 7) is considered one of the most promising building blocks for chemical synthesis (WERP T., G. PETERSEN, 2004), is also known as acid-oxopentanoic 4, 5-carbon molecule with a ketone group and a carboxylic. The presence of both groups increases the reactivity of the same for the synthesis of a wide range of other chemicals.

The preparation of the AL means controlled degradation of glucose, using the reaction when acids produced from lignocellulosic materials (GIRISUTA B., 2007) (Figure 8).



IUPAC name	4-oxopentanoic acid
CAS	(123-76-2)
Formula	$C_5H_8O_3$
Density	1.1447 g/cm^3
Boiling Point	245 °C a 246 °C
Melting point	33 °C a 35 °C

FIGURE 7 Properties and structure of acid Levulinic.

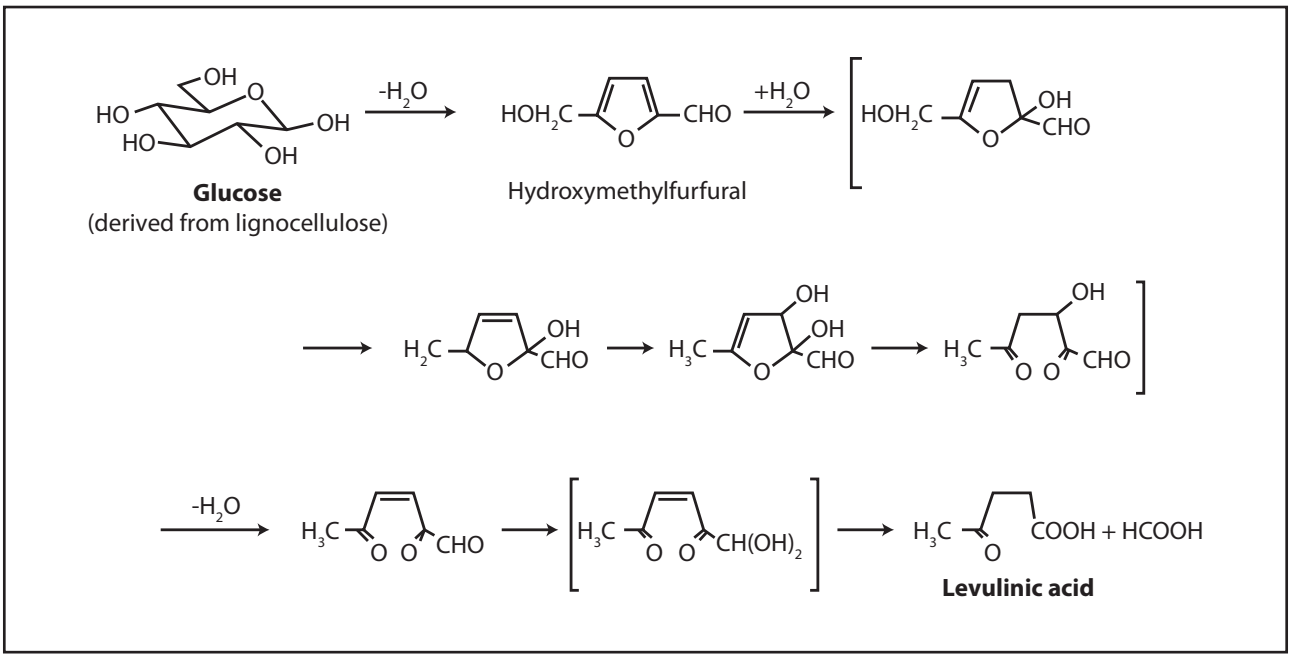


FIGURE 8 Sinthesys of levulinic acid.

According to NREL using this acid as a precursor chemical advantages, as it is a simple preparation, fast and with high yield and low production cost (U.S. $ 4-6/lb). Other authors pointed out the reaction low incomes (close to 70% of theoretical yield) and difficulty in separation. Another difficulty could be the lack of chemical operations from AL, necessitating the development of new chemical routes for the replacement of aromatic compounds and cyclic.

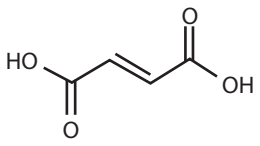
Dicarboxylic acids: fumaric acid

The fumaric acid (Figure 9), as well as succinic and malic acids are diacids that serve as precursors of several routes to obtain other specialized materials and commodities. Reduction reactions of fumaric provide butanediol, tetrahydrofuran and gamma-butyrolactone. The potential of diacids as building blocks is huge, studies suggest that effort should be made to obtain fermentation with minimum productivity of 2.5 g/Lh for the process economically feasible (WERP T., G. PETERSEN, 2004).

Studies were carried out in Brazil from hydrolyzed cassava (LETTER FS *et al.*, 1999), resulting in final concentrations of 21.3 g/L. It is possible to expect that similar results can be obtained from lignocellulosic hydrolysates of sugarcane (fraction rich in glucose).

Lactic

The lactic acid can be found in two isomeric forms D-and L-or DL-racemic mixture (this is obtained by chemical synthesis). When produced by fermentation is possible to produce the desired stereoisomer according to the organism and culture conditions used. Its production has been known since the nineteenth century, reaching production in the past decade close to 40.000 ton/



IUPAC name	Levulinic acid
CAS	(110-17-8)
Formula	$C_4H_4O_4$
Density	1.635 g/cm^3
Melting point	287 °C

FIGURE 9 Structure and properties of fumaric acid.

year (DATTA R., HENRY M., 2006). Fermentation technology in the production of acid is well developed and uses a wide variety of substrates such as molasses, hydrolysed starch and glucose. In general the processes are anaerobic, with yields of 90 mass% and reaching final concentrations of 10% to 13% (LUO J. *et al.*, 2006).

In 2005, he filed a patent on the production of D-lactic acid from hexoses and pentoses derived from lignocellulosic hydrolysates. It was described in this patent production by a bacillus wild (non-recombinant) able to grow and ferment different carbon sources (sucrose, fructose, glucose, xylose, arabinose, mannose, galactose and cellobiose) (SHANMUGAN *et al.*, 2005).

The lactic acid market is booming thanks to its recent applications in the polymer industry, hence the need to develop processes based on abundant raw materials derived from lignocellulose. In Brazil, studies have been developed production from lignocellulosic hydrolysates of malting (MUSSATI SI *et al.*, 2008).

Acrylic Acid

Studies on the feasibility of the biotechnological production of acrylic acid from sugar were described by STRAATHOF, AJ *et al.*, 2005 in the work group ttfranco (Unicamp). These authors suggested that metabolic and genetic engineering should be used to establish the real achievement of acrylic acid on an industrial scale from renewable resources.

Utilization of hemicellulose (xylose)

One of the derivatives of xylose with the greatest potential furfural is produced by acid dehydration of xylose and subsequent closure of the ring, the furfural and three water molecules are produced in this process (Figure 10).

The chemistry of furfural is well known, which in the period of post-war was widely used in the production of derivatives such as furan, THF and adipic acid. Its greatest application in that period was the production of nylon 6.6 (Figure 10) procedure that could return to the bio but with raw material from renewable sources.

Functional foods

Xylooligosaccharides can potentially be used for the prevention of dental caries, reduction of serum cholesterol and stimulating the growth of probiotics (*lactobacillus* and *bifidobacterium*) in the intestinal tract (MENEZES and DURRANT,

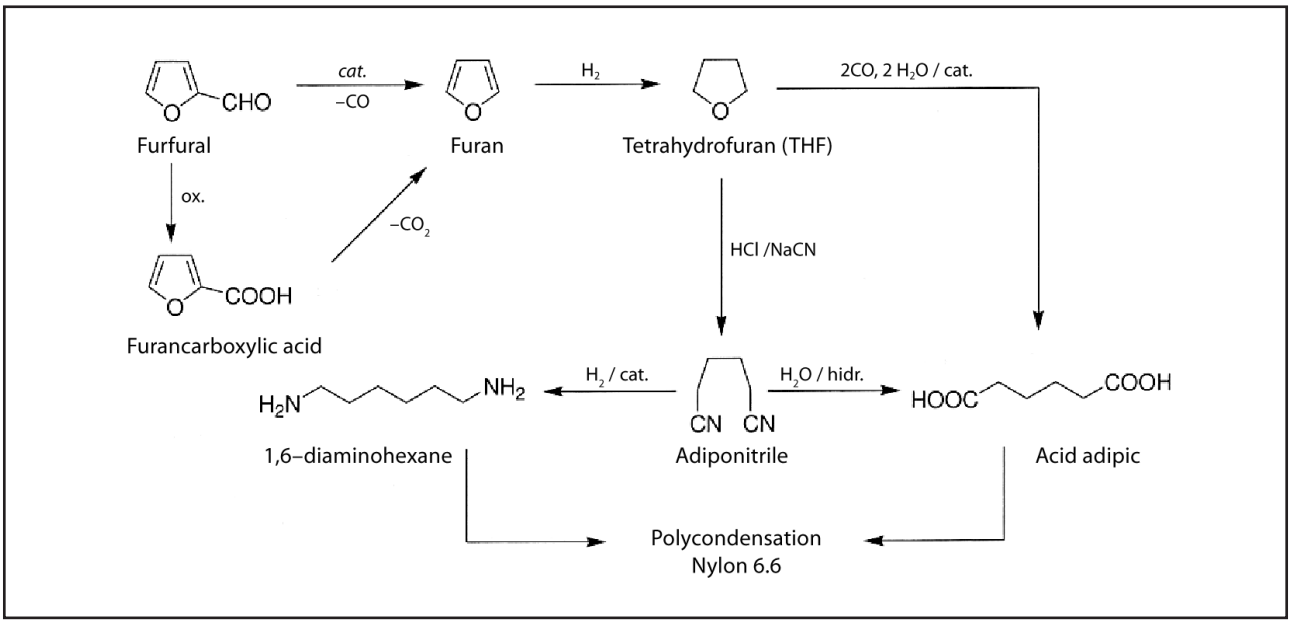


FIGURE 10 Derivatives of furfural.

2008). These compounds can be produced by enzymatic hydrolysis of lignocellulosic materials.

Xylitol

Xylitol is an alcohol-sugar sweetener with capacity similar to sucrose and lower caloric content (2.4 kcal/g compared with 4 kcal/g of sucrose). This sweetener has interesting features due to their commercial properties anticariogenic and metabolism independent of insulin. The production of xylitol can be done through two ways, through a chemical catalytic hydrogenation of xylose using nickel catalyst and high pressure. The second route, the biotech industry, using microorganisms of the genus Pichia sp. is now a reality. Processes based on hemicellulosic hydrolyzate of sugarcane bagasse have been described by the group of the Engineering School of Lorena (WHITE RF *et al.*, 2007).

CONSIDERATIONS AND SUGGESTIONS

The separation (fractionation) of biomass into its major components for subsequent processing is a major obstacle to the establishment of refineries and their development should be encouraged.

In the case of biomass from sugarcane, efficient processes for pretreatment, aimed at separating the cellulose from hemicellulose and lignin, and the different types of hydrolysis (acid, enzyme or in combination) should be encouraged to maximize the utilization of biomass. The lignin, are the two problems to be solved in the process of recovery: maintaining the natural structure of lignin and get it solubilized in high yields. The processes developed to date change to some degree the structure of lignin hindering the process.

Before the material discussed in this article, to obtain hydrolysates/depolymerized biomass with good quality and rich in hexoses and pentoses still needs to be improved, since many problems are still observed in this material, making the steps of fermentation, chemical and enzymatic catalysis.

Routes from glucose should be encouraged (because of their abundance) whereas other microorganisms known to be able to exploit this substrate well known routes and new routes should be encouraged.

Seen a huge deficit in the utilization of xylose, operating the routes that use it and the other pathway should be developed and encouraged as only known microorganisms that can metabolize this route. Other types of catalysts should also be encouraged.

Tools of genetic engineering and analysis of metabolic fluxes should be strongly encouraged to obtain a viable and economical route for obtaining chemicals from renewable sources. Development of fermentation processes, catalytic and chemical needs to be developed to achieve high concentrations and yields of desired biomolecules in line with the economic needs of industry. Integration of different tools will certainly be needed.

Routes to obtain biopolymers from building blocks (existing or brand new) need to be developed, given the huge deficit of polymers from renewable resources in industrial production. Simulation tools for metabolic processes and industrial processes, optimization techniques, modeling decision-making, exploration of "process systems engineering" should also be encouraged to reduce the development time of obtaining the necessary knowledge.

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