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Integrated Processes for Use of Pulps and Lignins Obtained from Sugarcane Bagasse and Straw

A Review of Recent Efforts in Brazil

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Abstract

Sugarcane bagasse and straw can be converted into pulps, oils, controlled-release formulations, chelating agents, and composites. This article reviews bagasse and straw conversion efforts in Brazil. Laboratory-scale processes were developed aiming at the integral use of these biomass byproducts. Organosolv pulping and oxidation of lignin are the most promising processes for the rational use of sugarcane residues. Fungal pretreatment and spectroscopic characterization are also discussed.

Index Entries: Integrated processes; sugarcane bagasse; lignocellulosic residues; Organosolv pulping; biomass pretreatment; spectroscopic characterization.

Introduction

The production of biomass in Brazil is higher than 20×10^9 t/yr, and calculations have shown that only 1% is necessary to replace the petroleum consumed in the country without impacts on the food and feed production or even damage to the native forests *(1)*. Integral utilization of this biomass (and not simply using part of it) is the more rational way to promote an alternative use of this high-value raw material. In the case of Brazil, regional particularities should also be taken into account. For example, in southeast Brazil sugarcane is widely cultivated but in the south the main crops are soybean and rice. In the northweast there are smaller and local harvestings of cacao, sisal, palm trees, and others.

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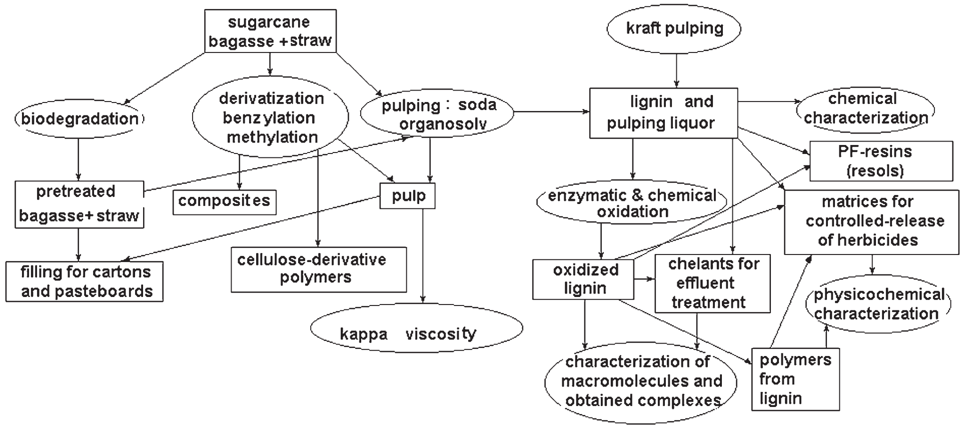

Fig. 1. Integrated processes for conversion of sugarcane bagasse and straw.

With respect to sugarcane, the main residues and byproducts are bagasse and straw, defined here as the leaves of the sugarcane. Environmental concerns and legislation will forbid from 2005 onward in São Paulo State the burning of sugarcane fields prior to harvesting. A great amount of sugarcane straw therefore will be available for use. This material has not been used as a source of chemicals, only as solid fuel.

Almost all products obtained from petrochemical processes can be obtained from biomass through direct, catalytic, or aggressive conversion of cellulose, hemicellulose, and lignin. The conception of an integrated process should take into account many factors, such as the industrial and academic interest for the study of synthetic routes. In our vision, summarized in Fig. 1, the integration of the processes was driven by the availability of residues from the sugar and alcohol industry and by the experience of our group in the last 10 yr.

Characterization of Raw Material

The composition of sugarcane bagasse is 43.7% cellulose, 24.4% hemicellulose, 28.0% lignin, and 0.75% ash. Spectroscopic techniques were developed for the characterization of this and other lignocellulosics because of the high versatility of the technique and additional information obtained. For example, nuclear magnetic resonance was applied to elucidate the structure of piassava lignin (a palm tree) *(2,3)*, and Fourier transform infrared (FTIR) spectroscopy has been successfuly used in the classification of lignins *(4)*.

General Results Concerning the Adopted Integrated Process

Sugarcane bagasse was pretreated with the white-rot fungi *Panus tigrinus* and *Ceriporiopsis subvermispora*, and 10% delignification and 15%

selectivity were obtained *(5).* Characterization of the fungal growth and of the obtained pulps has also been published *(6,7).*

Organosolv pulping became an interesting activity for the integrated processes. Acetosolv pulping of sugarcane bagasse furnished pulps with low lignin content but with low viscosity (12 cP). Enzymatic bleaching with xylanases was performed on these pulps, showing significative decrease in the residual lignin *(8).* Pulps can be used for the production of cellulose derivatives (with low hemicellulose content). Ethanol/water pulping of both sugarcane bagasse and straw has been utilized, with κ number reaching 13, with no effect on xylan present in the pulps *(9).* Pressure effects were investigated, showing a correlation between drastic conditions and depolymerization *(10).* The effects of the dose of xylanase on the bleachability of sugarcane bagasse ethanol/water pulps were also evaluated *(11).*

Integral use of lignocellulosics presents the difficulty of offering only the fuel alternative for lignins. On the other hand, lignin can be converted into phenolic oils by hydrogenolysis in a closed reactor and using microwave and ultrasound as pretreatments *(12).* Conversion reached 51% and the oil contained guaiacol and syringol and yielded 25%, as seen in Table 1. Dependence on lignin source and the amount used in the reactor were also investigated.

Controlled-release formulations of herbicides can also be obtained from lignins. This study has been developed in our research group in the last 15 yr, and the aim is the direct application of industrial lignins in the macromolecular state (without modifications) for the controlled release of herbicides in soil, in order to decrease their environmental impact. Recently, the mathematical modeling of such formulations was reported in four studies *(13–16).*

Oxidation was proposed as a suitable process for the modification of lignins. Chemical oxidation with O_2 using catalysts (cobalt and manganese salts) in alkaline and acidic conditions was performed in a simple three-necked round-bottomed flask. Kinetics showed a pseudo-first-order mechanism, and activation energy was 9 kJ/mol with catalyst, which increased to 15 kJ/mol without catalyst *(17).* This study was extended to the enzymatic oxidation with polyphenol oxidase (a laccase) and the oxidized lignins evaluated as chelating agents (metal scavengers) in the treatment of effluents containing heavy metals *(18).* More than 70% of the amount of metal was removed through the formation of chelates, as shown in Fig. 2, using copper ion as an example.

Integral use of lignocellulosics without separation of the components was directed to obtaining composites using integral fibers (sugarcane bagasse and straw) and also cellulose obtained from these raw materials *(19,20).* Mixing with polypropylene resulted in composites with similar or better mechanical properties than the crude polymer, but with lower costs owing to the high availability of lignocellulosics *(21).*

Table 1
Conversion and Oil Yields Resulting from Hydrogenolysis of Hydrolytic Lignins

Experiment no.	Lignin source	Lignin mass (g)[a]	Pretreatment	Conversion (%)	Oil yield (%)
1	Hydrolytic	84.16	None	41.3	27.6
2	Hydrolytic	84.13	Microwave	41.6	31.4
3	Hydrolytic	84.16	Ultrasound	35.2	22.0
4	Mildly hydrolytic	43.86	None	47.9	22.7
5	Mildly hydrolytic	43.88	Microwave	50.5	25.2
6	Mildly hydrolytic	87.72	Microwave	50.2	28.0
7	Mildly hydrolytic	87.75	Ultrasound	46.9	27.1

[a]Water and ash free.

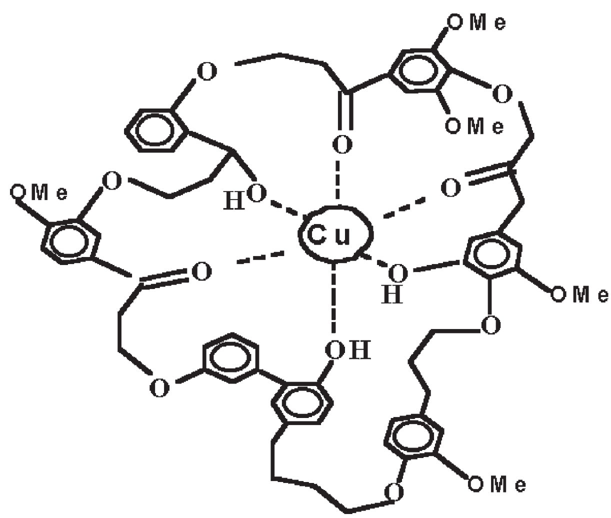

Fig. 2. Schematic structure formed after complexation of oxidized lignin with copper ion.

Complex structures should be characterized not only by chemical methods but also by modern spectroscopic analysis combined with mathematical tools, such as FTIR spectroscopy and principal component analysis (FTIR-PCA). Reaction of lignins in the formation of phenol-formaldehyde resins *(22,23)*, polymerization mechanisms *(24)*, and classification of pulps and distinguishing between pretreatment and bleaching processes *(5–8)* are examples of applications of FTIR-PCA.

Perspectives

We have shown that it is possible to consider the integration of processes utilizing biomass, even in a laboratory scale. We feel that the more promising applications will be those utilizing lignocellulosics in their macromolecular form, with only mild modification by oxidation and hydrolysis. Total conversion in low-molecular compounds should also be considered, but this will be achieved only with a combination of chemical and biologic/enzymatic processes.

Easy availability and consistency of biomass are important. In Brazil, especially in São Paulo State, sugarcane straw will become very abundant in the next 2 or 3 yr owing to environmental legislation. Attention should be directed to this fact. Alternative sources of fuels and chemicals are the main objective of the yearly National Renewable Energy Laboratory and Oak Ridge National Laboratory biotechnology symposia, and Brazil has the privilege of abundant biomass production. However, for fuels alcohol is produced directly from sucrose, and cellulose conversion has not been considered a strategic alternative, as it has in the United States.

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