DISSOLVING PULPS BY OXIDATION OF THE CELLULOSIC FRACTION OF LIGNOCELLULOSIC WASTE

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In memory of Acad. Cristofor I. Simionescu,
10 years after his passing, for his contributions
to the cellulose science and the creation of this prestigious journal

Cellulosic fractions of *Eucalyptus* sp. sawdust pulp and of sugarcane bagasse pulp, which had been subjected to hydrothermal and alkaline treatments, were purified by oxidative means (oxygen and ozone, followed by an alkaline extraction) to obtain dissolving pulp. The properties of the obtained pulps were evaluated and compared with those of commercial dissolving pulps. Eucalyptus sawdust pulp achieved 70% delignification after oxygen treatment and a kappa number of 5.8. Sugarcane bagasse pulps achieved 83% delignification and a kappa number of 8.7. Intrinsic viscosities within the range of specifications for dissolving grade pulps were obtained in the experiments on eucalyptus sawdust pulp. Higher values than required were obtained for sugarcane bagasse pulp. Retention values in 18% alkali were within the range of specifications for dissolving grade pulps, the highest values being obtained for alkaline extraction in the absence of hydrogen peroxide. Hydrogen peroxide addition in alkaline extraction produced high solubility values in both kinds of pulps.

Keywords: *Eucalyptus* sp. sawdust, sugarcane bagasse, dissolving pulp, biorefinery

INTRODUCTION

Forest biorefinery consists in the processing of lignocellulosic resources to produce energy, biomaterials and biochemicals. Biorefineries allow the use of renewable resources, taking advantage of the large amounts of agroforestry waste generated in the primary industrialization of wood or in agroindustrial processes.[1] Sugarcane bagasse is a lignocellulosic waste from sugarcane production. This waste is usually burned to produce heat and energy,[2] but sometimes it is over produced and stored. Similarly, the *Eucalyptus* sp. sawdust is a lignocellulosic waste from primary wood industrialization, but it is usually burned in sawmills in the open air producing pollution. An alternative would be the fractionation of these raw materials and the use of their components to generate high value added products.[3,4] The main structural components, such as cellulose, lignin and hemicelluloses, and eventually, the minor components, such as extractives and ash, can be can be utilized for this purpose.

Dissolving pulps represent a small fraction of the market and include viscose and high grade alpha cellulose for the production of acetates, ethers and other specialties.[5] End-uses of dissolving pulp include staple and filaments from regenerated fibers, films and sponges from cellophane, tow and plastics from cellulose acetate and pharmaceutical molding powder from microcrystalline cellulose.[6]

Wood cost, which often determines the competitiveness of a pulp manufacturing plant, typically varies between 40-65% of the total production cost, depending the product grade and the costs of chemicals, energy, and labour.[7] Most sawdust fibers are broken, being inadequate for making pulp for paper. Nevertheless, it is a very economical raw material to make dissolving pulp,

increasing the added value that can be obtained from this waste. Bagasse is also attractive for obtaining a product of greater added value, thinking primarily of productions at a lower scale than those required from pulp for paper mills.

Compared with paper grade pulp, dissolving grade pulp has a low amount of hemicellulose, lignin, extractives and minerals, higher brightness and more uniform molecular weight distribution.[8] The increasing interest in dissolving cellulose pulp that has been witnessed in recent years may be attributed to the growth in regenerated cellulose production.[9] Moreover, dissolving cellulose pulp may be used in nanofibrillated cellulose production.[10]

The use of sequential fractionation may be a possibility to separate the main components from lignocellulosic biomass and to achieve a purified cellulosic fraction.[11] Bleaching processes help remove almost all the residual lignin that is still present in the pulp after the delignification stage. Previous studies have focused on delignification using different bleaching sequences.[12,13] Sequences include chlorine stages, such as sodium hypochlorite, sodium chlorite and chlorine dioxide,[14,15] or totally chlorine-free stages, such as hydrogen peroxide, sodium hydroxide, oxygen, ozone and enzymes.[16-21] Oxidative methods, which are included in totally chlorine free stages, have attracted attention as they are considered more environmentally friendly.[22]

The aim of this work was to produce dissolving pulp by optimizing the purification of the cellulosic fraction from lignocellulosic waste by oxidative treatments (*Eucalyptus* sp. sawdust and sugarcane bagasse pulps obtained by a hydrothermal-alkaline fractionation sequence).

EXPERIMENTAL

Raw materials

The fraction of *Eucalyptus* sp. sawdust passing through an 18 mesh sieve (1 mm) and retained on an 80 mesh one (0.15 mm), obtained from a sawmill-carpentry company, was used as one of the lignocellulosic raw materials. The sawmill industrializes 12-50-year-old *Eucalyptus grandis*, *Eucalyptus saligina* and *Eucalyptus rostrata*. Sugarcane bagasse, the other fibrous waste, was supplied by a local mill (San Javier Sugar Mill, Misiones, Argentina). The bagasse pith was removed in two stages. In the former, bagasse was wet-depithed to break its structure in a Bauer disc refiner (plate gap of 0.01 in), after which the bagasse pith was removed by screening, using a plate with 2 mm wide slits (Wenmber). *Eucalyptus* sp. sawdust and sugarcane bagasse were subjected to hot water treatment at 180 ºC for 20 min.[23,24]

Both materials were then subjected to alkaline soda/anthraquinone cooking. The cooking conditions for *Eucalyptus* sp. sawdust were the following: 30 min at 170 ºC with 20% NaOH on oven dry (o.d.) wood, 0.1% AQ on o.d. wood, and liquid/sawdust ratio of 5.7/1. The conditions for the bagasse were as follows: 30 min at 175 ºC, 14% NaOH on o.d. bagasse, 0.05% AQ on o.d. bagasse, and liquid/bagasse ratio of 10/1.

Table 1
Conditions of cellulose purification stages

Trial	Sulfuric acid pretreatment	Oxalic acid (ppm)	Ozone stage time (min)	H_2O_2* (% on o.d. pulp)
T1	--	--	30	--
T2	--	--	30	0.5
T3	--	--	60	--
T4	--	--	60	0.5
T5	--	0.5	60	--
T6	--	0.5	60	0.5
T7	--	--	90	--
T8	--	--	90	0.5
T9	--	--	30	--
T10	--	--	30	0.5
T11	--	--	60	--
T12	--	--	60	0.5
T13	X	--	60	--
T14	X	--	60	0.5
T15	--	--	90	--
T16	--	--	90	0.5

*NaOH (2% on o.d. pulp) in all experiments

The final pulps had kappa number values of 19.4 for *Eucalyptus* sp. sawdust pulp and 52 for sugarcane bagasse pulp.

Oxygen treatment

Oxygen stages were conducted in a multipurpose reactor, equipped with a high shear rotor that generates the necessary agitation conditions, an inlet for oxygen and a heating system. The pulps were treated with a 3% NaOH charge on o.d. pulp, 0.1% $MgSO_4$ on o.d. pulp at 10% consistency, 100 °C for 60 min, and oxygen pressure of 6 kg/cm^2.

Ozone stage and alkaline extraction

Ozone treatments were performed in a rotary evaporator equipped with a device for bubbling ozone into the system. The fixed conditions for the ozone treatment were the following: pH 2.3, temperature of 25 °C, O_2 flow of 0.5L/min and consistency of 1.5%. After ozonation, the samples were thickened by filtration, washed by dilution to 1% consistency and then thickened to 20% consistency.

Sulfuric acid pretreatment (at 95 ºC and pH 3 during 100 min) and oxalic acid addition (0.5 ppm) were tried to verify their influence on the ozone stage.

The alkaline extraction stage consisted in the application of 2% NaOH on o.d. pulp, alone and reinforced with hydrogen peroxide (0.5% H_2O_2 on o.d. pulp). The extraction was performed under the following conditions: consistency of 10%, temperature of 80 °C, during 60 min. Variable conditions are shown in Table 1.

Characterization of purified cellulose

The obtained pulps were characterized in terms of brightness (ISO 3688), using a Color Touch Spectrophotometer (Technidyne Corporation), kappa number (Tappi Standard Method T236 om-99), alkali solubility (TAPPI Standard Method T235 cm-00) and ash content (Tappi Standard Method 211 om-02).

Measurements of intrinsic viscosity were carried out according to ISO 5351/1-1981(E). To determine the crystallinity index, Phillips X'Pert diffraction equipment with Cu radiation was used. Diffraction was performed in the stepwise scanning mode with a scan speed of 0.02° (2θ)/min in the range of 40 to 5 degrees (2θ). Statistical analyses were performed with 95% significance.

RESULTS AND DISCUSSION

Oxygen delignification

The oxygen stage achieved 70.1% delignification for the *Eucalyptus* sp. sawdust pulp (kappa number of 5.8) and 83.3% delignification for the sugarcane bagasse pulp (kappa number of 8.7).

The delignification achieved by the oxygen treatments was higher than the values reported in the literature for hardwood. For example, previous studies showed that one or two-stage oxygen delignification can remove 35-50% of lignin from a hardwood kraft pulp, and 40-70% from a softwood kraft pulp.[25-28] Kappa numbers were higher than those obtained by Schild *et al*.,[29] for eucalyptus pulp, and also higher than those obtained by Freitas Andrade and Colodette,[30] for sugarcane bagasse pulp.

The crystallinity indexes obtained were of 87.7% for the *Eucalyptus* sp. pulp and 86.4% for the sugarcane bagasse pulp, and were similar to those reported by De Souza *et al*.[31]

Ozone stage and alkaline extraction

The eucalyptus sawdust pulp consumed 4.3% of ozone on o.d. pulp in 90 minutes, whereas the sugarcane bagasse pulp consumed 1.3% on pulp in the same period of time. Increased consumption of ozone at longer exposure times is expected for both raw materials.

Cellulose purity requirements for dissolving pulps are higher than those for paper pulps. Dissolving pulps are sold according to solubility in sodium hydroxide (S18 or S10 values), content of impurities, such as resin components and inorganic material, viscosity, brightness and kappa number.[32] These pulps also require a certain level of viscosity, high brightness and high reactivity to specific chemicals. The specifications of some dissolving pulps found in the literature are indicated in Table 2.[33,34]

The cellulose content in a pulp depends on the raw material and the process used. For the sulfite process (AS) pulp from any raw material, it varies in the range of 87-96%, whereas for a pulp obtained by a sulfate process with prehydrolysis (PHK), it varies in the range of 93-98%.[33] The higher values for the cellulose content of PHK pulp, with respect to that of AS pulp, are due to differences in the chemistry of both processes, since the main mechanism for carbohydrate degradation in the AS process is acid hydrolysis, whereas in the PHK process is alkaline peeling.[35] Acid hydrolysis is more effective than alkaline peeling in decreasing the molecular weight of cellulose, and some low molecular weight structures could be dissolved when determining the cellulose content.

Hydrogen peroxide addition in alkaline extraction significantly reduces the viscosity of eucalyptus sawdust pulp and sugarcane bagasse pulp ($p = 0.00$). Such a noticeable decrease in viscosity is due to the formation of free radicals

by decomposition of hydrogen peroxide under alkaline conditions. Free radicals attack the carbohydrates, decreasing viscosity, as has already been shown by Freitas Andrade and Colodette.[30]

The intrinsic viscosities of the treated eucalyptus sawdust pulps were in the range required by the specifications for dissolving grade pulps shown in Table 2, in the case when no hydrogen peroxide was added (T1, T3, T5, T7). For bagasse, they were even higher (experiments T9, T11, T13 and T15). Intrinsic viscosity must be maintained between 200-600 mL/g, since it is reduced to 200 mL/g during the aging step of the viscose process.[35,36] If viscosity is too low, filtration becomes difficult during the viscose process and affects the strength of final fibers. On the contrary, if viscosity is too high, it will cause problems during mercerization and xantation.[37]

On the contrary, the addition of H_2O_2 in alkaline extraction, as well as ozonation time, increased pulp brightness significantly in both cases (p=0.00 and p=0.01 for the eucalyptus sawdust pulp and the sugarcane bagasse pulp, respectively). Lower brightness values than those required by dissolving grade pulp specifications were obtained. The highest brightness obtained was 84.6% ISO for the eucalyptus sawdust pulp and 79.5% ISO for the sugarcane bagasse with 90 minutes of ozonation time and alkaline extraction reinforced with hydrogen peroxide. These results are similar to those reported for the Acetosolv process followed by TCF bleaching.[38]

Retention in 18% (R18%) alkali represents the product yield of an alkaline process for the production of viscose fibers or cellulose ethers. Dissolving pulps require high values of R18%, since it represents the percentage of high molecular weight cellulose in pulp. Generally, the specifications of dissolving pulps include α-cellulose instead of retention in 18% or 10% alkali (R18% or R10%), but α-cellulose usually shows values between R10% and R18%.[39]

All the obtained values were within the range or superior to those of dissolving grade pulp specifications. Peroxide addition in alkaline extraction and ozonation time determined a decrease in the R18% value of eucalyptus sawdust pulp ($p = 0.00$), but there were no significant differences between ozonation durations of 30 and 60 minutes. The effect of the variables was much less noticeable in the case of sugarcane bagasse pulp.

Similar conclusions about the effect of the studied variables can be drawn for the R10% fraction. There was a positive correlation between the fraction R10% and viscosity ($r = +0.81$). The solubility value in 10% alkali (S10%) represents the percentage of hemicelluloses and low molecular weight cellulose in pulps. Peroxide in alkali extraction and ozonation time exerted a significant effect on S10% for eucalyptus sawdust pulp ($p = 0.00$ and $p = 0.04$, respectively), but there were no significant differences between durations of 30 and 60 minutes.

R10% values fell within the range of dissolving grade pulp specifications, being higher than those for the alkaline extraction without hydrogen peroxide. This variable also affected the S10% value of sugarcane bagasse pulp ($p = 0.00$). The obtained values of R10% confirm the formation of free radicals under the alkaline conditions in the alkaline extraction with a hydrogen peroxide stage.

Table 2
Dissolving grade pulp specifications

Parameter	Viscose hardwood sulfite pulp[33]	Viscose hardwood prehydrolysis kraft pulp[33]	Viscose eucalyptus prehydrolysis kraft pulp[32]
Intrinsic viscosity (mL/g)	500	450	400-550
Kappa number	0.3	0.3	<0.5
ISO Brightness %	93.0	89.0	88.0-90.5
R18 (%)*	95.0	96.5	>96.5
R10 (%)*	89.0	92.0	>92.0
Total ash (%)	0.10	0.08	<0.12

*R18 (%) and R10 (%): retention in 18% and 10% alkali, respectively

Table 3
Properties of pulps after the ozone stage and alkaline extraction

Trial	Intrinsic viscosity (mL/g)	ISO brightness (%)	Retention in 18% alkali (%)	Retention in 10% alkali (%)	Solubility in 10% alkali (%)	Kappa number
Eucalyptus sp. sawdust pulp						
O_2	621	52.7	97.3	92.1	7.9	5.8
T1	517	67.9	97.3	90.9	9.1	2.9
T2	375	72.3	96.7	87.8	12.2	2.6
T3	457	77.5	97.1	90.7	9.3	1.3
T4	356	82.0	96.7	87.5	12.5	1.1
T5	463	77.1	97.0	91.2	8.8	2.1
T6	350	81.9	96.7	89.0	11.0	1.1
T7	447	80.4	96.9	90.8	9.2	1.0
T8	340	84.6	96.3	88.4	11.6	0.7
Sugarcane bagasse pulp						
O_2	850	47.6	95.9	94.9	5.1	8.7
T9	764	58.5	96.9	94.4	5.6	4.6
T10	432	66.3	96.3	92.5	7.5	3.8
T11	693	71.8	96.5	93.9	6.1	2.1
T12	401	76.9	96.1	91.3	8.7	1.8
T13	790	72.4	96.9	92.9	7.1	2.1
T14	417	77.2	96.1	90.8	9.2	1.8
T15	780	75.1	96.7	92.9	7.1	1.8
T16	410	79.5	96.0	91.6	8.4	1.6

O_2: Pulp obtained in the oxygen stage

R18% and R10% values were always higher for eucalyptus sawdust pulps than for sugarcane bagasse pulps. R18 and R10% values for eucalyptus sawdust pulps reached standard specifications for cellulose acetate production.[39]

It has been reported that sulfuric acid treatment, previous to the ozone stage and oxalic acid addition, improves the selectivity for that stage.[16] Nevertheless, acid pretreatment had no effect on the studied properties of the pulps. On the contrary, oxalic acid addition decreased significantly the 10% alkali solubility of the pulps.

The residual lignin content influences negatively viscose production. Pulps with a kappa number > 2 have lignin contents that generate color, interfere with cellulose reactivity and also can precipitate, obstructing the tubes through which viscose fibers pass during spinning in the extrusion process.[40]

There were no significant differences in kappa number corresponding to ozonation periods of 60 and 90 minutes (even if the trend indicates a lower value for 90 minutes).

Bagasse pulps presented lower brightness and higher kappa numbers than eucalyptus sawdust pulps, which can be explained by the more condensed nature of lignin in the bagasse pulps. The p-hydroxyphenil groups in lignin are significant in grasses, being more recalcitrant to bleaching than other types of structures in lignin.[41] Differences could also be explained by the generation of oxalates during the bleaching process (as a result of hexenuronic acids present in hemicelluloses),[42] but, in this case, it is not probable because hemicelluloses were extracted in the preceding hydrothermal step. Total hemicelluloses extracted in the hydrothermal treatment for eucalyptus sawdust and sugarcane bagasse were of 79.6 and 81.7% of their initial content, respectively (residual hemicelluloses were 2.5% on o.d. wood pulp and 5.0% on o.d. bagasse pulp). Therefore, oxalate formation can be considered as negligible.

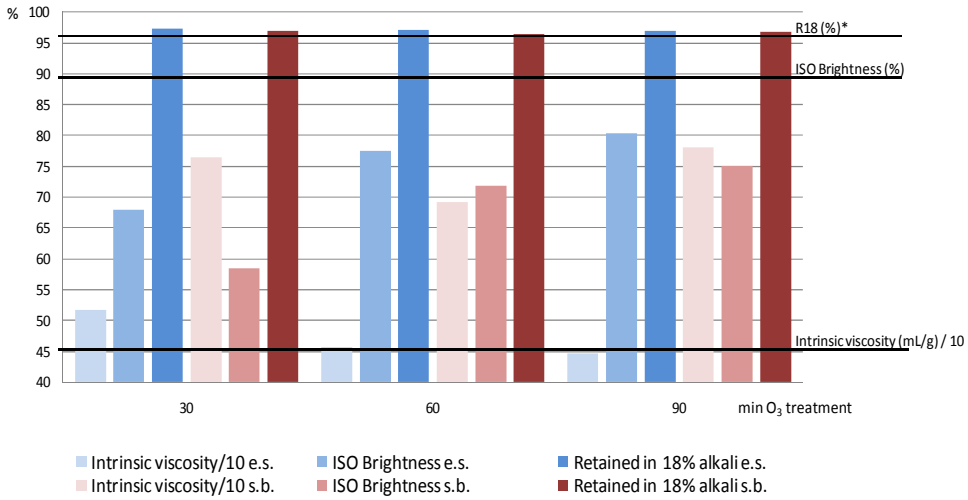

Figure 1: Comparison of properties of eucalyptus sawdust pulps and sugarcane bagasse pulps treated with ozone and alkaline extraction during different time periods (e.s.: eucalyptus sawdust pulp, s.b.: sugarcane bagasse pulp). Lines show reference values

Table 4
Crystallinity indexes of eucalyptus sawdust pulp and sugarcane bagasse pulp ozonized for 60 min

Trial	Crystallinity index (%)
T3	87.2
T4	88.2
T11	86.5
T12	85.7

Figure 1 shows the comparison of properties of eucalyptus sawdust pulps and sugarcane bagasse pulps treated with ozone and 2% NaOH during different time periods.

The usual way to obtain 98% purity dissolving pulp at industrial scale is by the kraft pulping process, with a prehydrolysis step and subsequent bleaching and alkaline purification.[43] A sulfite pulp with subsequent bleaching and an alkaline purification step achieves 96% purity. These two processes are applied to conifers, hardwoods and grasses.[44] A soda treatment at high temperatures followed by a bleaching step was also used to obtain dissolving pulp from cotton.[45] Another way to obtain dissolving pulp is by using paper grade pulp and enzymatic treatments. These include multi-component enzymes to increase the reactivity and accessibility of cellulose in the pulp to obtain dissolving grade pulp in a selective, effective and environmentally friendly manner.[7] The primary goal of the above treatments is to reduce the recalcitrance[46] and finally obtain a cellulose pulp with low lignin content. The values obtained in this work for eucalyptus sawdust and sugarcane bagasse pulps, by applying autohydrolysis, alkaline and oxidative treatments, were of about 96%.

Crystallinity indexes were analyzed in the pulps ozonized for 60 minutes without acid (Table 4). Crystallinity indexes are higher than those obtained in a prehydrolysis soda/AQ pulp with ECF bleaching,[47] and the pulps subjected to different processes of pulping and bleaching developed by Fink *et al*.[48]

The average ash content in the final pulps was 0.21% (sd = 0.03%) for the sugarcane bagasse pulp, and 0.24% (sd = 0.01%) for the eucalyptus sawdust pulp, slightly higher than the specified values for dissolving grade pulps, which can be attributed to the incorporation of inorganic impurities during the processing of wood at the sawmill. However, Barba *et al*.[49] suggested that carboxymethylcellulose can be produced from dissolving pulps with ash content values of about 0.7%. The ash values obtained in this work are lower than those obtained by Freitas Andrade and Colodette,[30] for sugarcane bagasse pulp and higher than those obtained by Ribas Batalha *et al*.[50] for eucalyptus pulp.

The potential of industrial biomass waste to yield dissolving pulps was evaluated. The use of a short sequence of delignification and bleaching gave acceptable results. The final kappa number could be reduced by decreasing the kappa number of the pulp entering the oxygen stage (cooking optimization), or by the incorporation of a second delignifying oxygen stage. These changes should increase delignification and brightness of the pulps.

CONCLUSION

Residues from agro/forest industries can be used to produce dissolving pulp using an environmentally friendly process.

It is worth noting that even when the quality of the pulp from eucalyptus sawdust is not adequate for producing commercial grade paper, it can be successfully used to obtain dissolving pulp of acceptable quality by the processes outlined in this paper.

Eucalyptus sawdust alkaline pulp achieved 70% delignification after oxygen treatment and a kappa number of 5.8. The consumption of ozone reached 4.3% o.d. pulp for the 90 min process.

Sugarcane bagasse alkaline pulp achieved 83% delignification and a kappa number of 8.7, while the consumption of ozone reached 1.3% on o.d. pulp.

Intrinsic viscosities within the range of dissolving grade pulp specifications were obtained in the experiments on the eucalyptus sawdust pulp. Higher values than the required ones were obtained for the sugarcane bagasse pulp. In the tests where alkaline extraction was reinforced with hydrogen peroxide, viscose grade values were reached.

For both kinds of pulp, the brightness values were somewhat lower than that of dissolving grade pulp specifications and retention values in 18% alkali were within the range of dissolving grade pulp specifications, the highest values being obtained in the tests on alkaline extraction in the absence of hydrogen peroxide. Eucalyptus sawdust pulps presented lower kappa numbers than bagasse pulps.

Acid pretreatment had no effect on the studied properties of the pulps, whereas oxalic acid addition decreased significantly the 10% alkali solubility of the pulps.

Hydrogen peroxide addition in alkaline extraction reduced kappa number and improved brightness. On the contrary, it produced high solubility values in both kinds of pulps. The only exception occurred in the experiments in which oxalic acid was added.

Ash contents of 0.21% for sugarcane bagasse and 0.24% for *Eucalyptus* sp. sawdust pulp were obtained, *i.e.* slightly higher than the specified values of dissolving grade pulps.

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