Improved Eucalyptus Pulp Bleachability Via High Temperature Acid Treatment

Edvins Ratnieks
Celso Foelkel
Vera Sacon
Moacir Sauer

RIOCELL S.A.

1. Introduction

This paper presents the key findings of the Riocell Technology Center to understand and develop the state-of-the-art technology of acid hydrolysis to decrease the kappa number of pulps . The Center has been studying specifically this phenomen since 1994. It takes part of a major development project to understand and improve the bleachability of the eucalyptus kraft pulp produced by the mill. The driving forces of this project have been the economical aspects of chemicals consumption, due to poor selectivity and reactivity, increasing production costs, chlorine gas elimination, and especially the kraft cook heterogeneity and its associated consequences.

Our first perception of the opportunities in the acid hydrolysis field are associated with the studies of the unbleached pulp leaching, presented as a mill case in the 1994 Latin American Delignification Conference (E. Ratnieks, V. Sacon, C. Zimmer, C. Foelkel). The findings were further on extended and presented in the 1995 TAPPI Pulping Conference (E. Ratnieks, C. Foelkel, V. Sacon, C. Zimmer). Both alkaline and acid effects were studied. We found at that time the results very promising to reduce the kappa number prior to the bleach plant.

The acid hydrolysis of pulps has been a known practice (G. Gellerstedt, E.-L. Lindfors, 1987) at least on how it affects lignin. An elegant explanation on how it affects the sugar polymers in the pulp has been recently given (T. Vuorinen, A. Teleman, P. Engenström, J. Büchert, M. Tenkanen, 1996).

One concern is the pulp yield and selectivity losses that come together with acid hydrolysis stages. This practical observation points out that multiple pulp structures undergo acid cleavage and water oxidation, no matter which chemical structure predominates.

The specific purpose of this paper is to present the results produced with the eucalyptus kraft pulp from our mill, regarding its behavior to acid hydrolysis and the solutions we provided to maximize the kappa number reduction, without excessive yield loss. A selection of eucalyptus pulps were also studied with respect to this behavior.

2. Current Status of Development

Our early studies on eucalyptus kraft pulps with respect to acid treatment were developed under the scope of the time and temperature variables that could alter the leaching of lignin. This means, some screening lab trials have indicated that temperatures above 100 ºC could produce some important changes on the kappa number of pulps. As the trials were targeting lignin removal and the kappa number was decreasing substantially, the acid hydrolysis treatment was thought to be promising. The Table 1 describes some of the results we have got in the beginning of our work.

"Trabalho apresentado no 30º Congresso Anual de Celulose e Papel da ABTCP, realizado em São Paulo - SP - Brasil, de 03 a 07 de novembro de 1997".

Table 1 - acid treatment of a eucalyptus oxygen delignified pulp

Treatment conditions	kappa number	intrinsic viscosity	yield
		cm^3/g	%
no treatment	9.1	880	-
70 °C; 300 min; pH 5.0	9.0	880	99
70 °C; 300 min; pH 3.0	9.0	880	99
115 °C; 10 min; pH 5.0	7.8	860	99
115 °C; 10 min; pH 3.0	7.5	850	99
115 °C; 20 min; pH 5.0	7.4	860	99
115 °C; 30 min; pH 5.0	7.3	830	99
120 °C; 60 min; pH 5.0	6.2	820	93
120 °C; 120 min; pH 5.0	5.8	800	92

Our first results have directed us to the kappa number reductions in temperatures beyond 100 °C, because we were looking for mechanisms related to the lignin dissolution and diffusion. Important kappa number reductions (>30%) are possible to achieve especially at 120 °C with a short retention time and mildly acidic pH. The sulfuric acid consumption to correct an oxygen delignified and washed pulp pH is about 1-2 % on oven dry pulp basis. The viscosity loss is acceptable, but the yield loss is severe. These first results were in line with other works (Y-P. Sun, K. Ngueyn, A. Wallis, 1995 and A. Marechal, 1993). This yield loss were not attributed to hemicellulose losses, as noted in our work and confirmed by the work of Sun (1995). The explanation for this behavior was described elsewhere (G. Gellerstedt, E.-L. Lindfors, 1987). The hypothesis discussed was the formation of new phenolic hydroxyl groups within the lignin molecules, dissolving and diffusing lignin out of the fibers. The tricky point to understand is why the yield decreases sharply, even at mildly acidic conditions as showed in our work. This question can not be derived from the early works, because their conditions to establish the acid treatment were clearly aggressive with respect to the acid charge, lending support to any kind of hydrolysis effects. The solution to the yield preservation is described in the Table 2.

Table 2 - effect of the acid two-stage approach (pH=3.0) on eucalyptus oxygen delignified pulp.

Treatment conditions	kappa number	intrinsic viscosity	yield
		cm^3/g	%
no treatment			
oxygen delignified pulp (mill sample)	10.5	960	-
one-stage			
60 min @ 120 °C	6.1	920	92
two-stage			
10 min @ 120 °C + 50 min @ 90 °C	6.1	900	99
two-stage			
10 min @ 130 °C + 50 min @ 90 °C	5.2	830	98

From the data above it is possible to derive that a combination of temperature and time above and below the boiling temperature of water could provide retention times of one

hour or less. The design of such reactors is well established and currently in use for several applications. To understand the magnitude of the variables involved, we present in the Table 3 an example taken from an extensive work with various eucalyptus pulps.

Table 3 - example of an optimization scheme for time, temperature and pH of the acid treatment. Initial kappa = 10.8; viscosity = 1000 cm³/g.

pH 2.0	pH 2.5	pH 3.0	(same pH conditions for the equivalent columns)
			one-stage 60`@90°C
k=7.3 v=870 y=99	k=7.4 v=910 y=99	k=7.5 v=900 y=99	two-stage 10`@120°C+50`@ 90°C
	k=9.4 v=950 y=99		one-stage 60`@90°C
k=6.0 v=820 y=99		k=6.4 v=890 y=99	two-stage 20`@120°C+40`@ 90°C
k=8.6 v=910 y=99		k=8.8 v=930 y=99	one-stage 90 min @ 90°C
	k=5.2 v=770 y=97		one-stage 90 min @ 120°C

k= kappa units

v= viscosity cm³/g

y= yield %

From the Table 3, it is possible to understand that the two-stage approach is a feasible option as the 20 minutes stage at 120 °C followed by an atmospheric 90°C stage of 40 minutes shows a 4.5-5.0 kappa units reduction (a 45% reduction) with good yield. It worths to mention that this simplified scheme is a display of the opportunities of the two-stage approach. Any combination of time and temperature are possible to suit the mill needs.

3. **Survey on Eucalyptus Pulps**

One critical question about this technology is how universal are the findings and the extension of this behavior on other eucalyptus kraft pulps. We have sampled pulps from some mills in South America and from a selection of these, we are able to discuss some interesting points. The Table 4 displays data from the acid treatment used at constant conditions that we believe can produce a near maximum effect in the kappa reduction. The results are organized according to the digester technology, in the ascending order of the installation year. A separate finding is discussed to the two conventional batch digesters shown in Table 5. We assume that a significant finding in such a short survey must be show a 10^{+}% relative difference. All figures are rounded off, for easy comprehension and assuming the stipulated relative error.

Table 4 - kappa reduction for the eucalyptus oxygen delignified pulps in the acid treatment constant conditions: 20 min @ 120 °C + 40 min @ 95 °C; pH = 2.5

PULPS SAMPLED AFTER THE OXYGEN DELIGNIFICATION WASHING STEP				
	kappa reduction	viscosity reduction	Δviscosity/Δkappa ratio	digester technology (sorted in ascending order of installation year)
Mill	Δ units	Δ cm^3/g		
A	4.5	140	35	MCC®
B	4.5	140	35	MCC®
C	4.5	110	25	MCC®
D	5.0	125	25	ITC®
E	4.5	90	20	Batch
F	3.5	50	15	Batch

Table 5 - kappa reduction for eucalyptus kraft pulps in the acid treatment constant conditions: 20 min @ 120 °C + 40 min @ 95 °C; pH = 2.5

PULPS SAMPLED AFTER THE DIGESTER WASHING STEP (MCC TECHNOLOGY)				
	kappa reduction	viscosity reduction	Δviscosity/Δkappa ratio	digester technology (sorted in ascending order of installation year)
Mill	Δ units	Δ cm^3/g		
A	4,0	220	55	MCC®
B	2,5	160	65	MCC®
C	5,0	180	35	MCC®

The optimized acid treatment show near constant results of the kappa reduction for the digesters using the continuous cooking technology. It is possible to assume it is applicable to many mills using the eucalyptus wood. Although it works with the batch cooking technology, its extension is not so pronounced within the set of samples we have taken. One interesting point to discuss is the selectivity of the acid stage, according to the Δviscosity/Δkappa ratios observed. They qualitatively correspond to the technology of the digester, mainly due to the age of the continuous digester. The older the technology, the worse the selectivity. The closer to the digester the sampling is (as shown for the three MCC digesters in Table 5), the greater the dispersion and the poorest the kappa number reduction. The ITC® digester displays the best performance on the selectivity of the acid stage. Interestingly, the old conventional batch digesters have a similar or better selectivity. What could be the lost link between so distinct technologies?

From a parallel work performed by our Technology Center on the pulp bleachability due to the continuous digester operation mode, one can dare to produce a rational explanation, yet difficult to prove directly. From the observation of the temperatures of the digester shell it was learnt that these temperatures correlate with bad mixing and poor liquor circulation in the upper section of an early 70's continuous digester. In the ever evolving technology of cooking, this fact has been overcome by the design of new chip feeders,

screens and installation of a trimming circulation, with strict controls of flows, alkali profiles and sulphidity. The old generations of digesters are not so sophisticated and operate the top section at rather heterogeneous conditions. This is aggravated by the operation at overcapacity of the great majority of these old digesters. The result is that the top section temperatures have been raised to increase cooking capacity. And so does cooking heterogeneity. This is easily seen in the dynamic computational modeling provided by the vendors of the technology. We have used the proprietary CROSSIM software from Kvaerner Pulping. From the fundamental knowledge, such variations in the kappa number in the cross section of the digester in the beginning of the bulk delignification phase can no longer be corrected due to the restricted regimen of chips flow through the vessel. This operation abnormality produces a dispersion of the outcoming kappa number from the digester. The modern digesters have a greater amount of circulation loops to solve this, and not surprisingly, the old conventional batch systems do not suffer from these abnormalities.

As a result, a pulp from the old generations of continuous digesters present a wide distribution of lignin among the fibers and also within the same fiber. This enables the speculation that the acid accessibility to the hydrolyzable structures within the fiber ultra-structure is much more difficult, due to the presence of localized lignin. This model can be thought as a stereo-physical barrier either to access and remove sugar and lignin fragments or to transform them, due to difficult accessibility of the acid solution. As the acid treatment can overcome these barriers with adequate time, temperature, ionic strength or a combination of them, with characteristic selectivity according to the origin of the pulp, it is impossible to think of a highly selective hydrolysis occurring. It is simply acid hydrolysis of the fiber structure.

4. Installation Examples

Considering that a mill wants to make a bleach plant retrofit to improve its production of ECF grade, what would be the expected chemicals consumption for the different ECF approaches available? The following topics will discuss the opportunities with chemicals savings and also some aspect of the bleach plant costs.

4.1 ECF with chlorine dioxide, hydrogen peroxide and oxygen

The Table 6 displays the opportunities in saving chlorine dioxide by the simple add-up of the acid stage and both the acid stage and bleach sequence re-configuration. The simple addition of the acid stage enables a proportional chlorine dioxide reduction. Further sequences changes, as its shortening or peroxide re-enforcement show gains or losses proportional to the further changes introduced.

In this specific case there is no indication that any of the structures modified or extracted by the acid treatment enhance the use of chlorine dioxide, peroxide or oxygen. The chemicals reduction is according to the kappa number reduction for the case of the chlorine dioxide and in the case of oxygen and peroxide re-enforced extraction they replace proportionally an amount of the chlorine dioxide necessary.

Table 6 - ECF chemicals consumption (100% chlorine dioxide) of an oxygen-delignified pulp with the acid (A) stage. "A" stage conditions: 20 min @ 120 °C + 40 min @ 95 °C; pH = 2.5; kappa incoming to the "A" stage: 9.5; kappa outcoming of the "A" stage: 5; 90.5% ISO final brightness

Bleaching sequence	Chemicals consumption		
	ClO_2	H_2O_2	act. Cl. Savings
	act. Cl. Kg/ADMT	kg/ADMT	%
(D0)(E1)(D1)(E2)(D2)	56	-	0
(A)(D0)(E1)(D1)(E2)(D2)	35	-	38
(A)(D0)(EO)(D1)(D2)	38	-	32
(A)(D0)(EOP)(D1)(D2)	32	3	43

4.2 **ECF with ozone, oxygen, hydrogen peroxide and chlorine dioxide**

The ozone and peroxide-enhanced bleaching sequences are very sensitive to the acid stage. The savings in the ozone and peroxide charges increase sharply and the bleach plant can be retrofitted to a "mini-TCF" one, due to the low amount of chlorine dioxide necessary. The (DZ) stage also works fine together with the acid treatment, decreasing the amount of ozone necessary. The strong interdependence of these acid stages give rise to the thought that most of the consumption of acid oxidants are due to an "acid background effect".

Table 7 - Chemicals consumption in the ECF bleach plant (chlorine dioxide, ozone, hydrogen peroxide, oxygen) of an oxygen-delignified pulp with the introduction of the acid (A) stage. "A" stage conditions: 20 min @ 120 °C + 40 min @ 95 °C; pH = 2.5; incoming kappa to the "A" stage: 9.5; outcoming kappa of the "A" stage: 5; 90.5% ISO final brightness

Bleaching sequence	Chemicals consumption			
	ClO_2	O_3	H_2O_2	act. Cl. Savings
	act. Cl. Kg/ADMT	kg/ADMT	kg/ADMT	%
(D0)(E1)(D1)(E2)(D2)	56	-	-	0
(Z)(EOP)(D)	30	5.0	5.0	46
(A)(Z)(EOP)(D)	13	4.5	4.5	77
(A)(DZ)(EOP)(D)	13	2.5	4.0	77

5. **A Mill Case Study (ECF with 100% chlorine dioxide and oxygen)**

From the data shown for the several bleaching sequences presented, it is natural to understand that the chemical consumption can be decreased substantially with the use of the acid stage. We understand that each mill sees one opportunity with different points of view. In

the Table 7 we summarize the bleach plant costs calculated for both the single-stage and two-stage options. The simplest comparison is made for a 100% chlorine dioxide bleaching option, enhanced by oxygen re-enforcement in the alkaline extraction.

The savings of chlorine dioxide are mainly compensated or exceeded by the costs of the steam necessary to balance the acid treatment conditions. This means that this option has scarce possibility in reducing the bleaching specific cost. An increase in bleaching capacity, a shortage in chlorine dioxide production and the need to abandon the use of chlorine gas are the natural justifications for such retrofit option. It gives the opportunity to keep the bleach plant simple, without the introduction of exotic chemicals into the mill, and in case of their use, to decrease the dependence of external supply, which sometimes is a logistics problem.

Table 7 - bleach plant costs with the acid treatment installed either as a two-stage or as a single- stage reactor. Incoming kappa to the "A" stage: 9.5; outcoming kappa of the "A" stage: 5; 90.5% ISO brightness

		bleach plant specific costs, US$/ADMT		
Bleaching sequence		(D)(E)(D)(E)(D) base case	(A)(D)(EO)(D)(D) two-stage 20'@120 °C+40'@95 °C pH 2.5	(A)(D)(EO)(D)(D) single-stage 300'@98 °C pH 3.5
Chemicals	NaOH	2.66	3.37	3.37
	ClO_2	21.95	12.85	12.90
	SO_2	0.40	0.48	0.48
	H_2SO_4	0.00	1.90	1.12
	O_2	0.00	0.40	0.40
Total 1		25	19	18
Utilities				
	Steam	2.84	12.86	9.86
	Energy	4.74	4.62	4.62
	Water	0.36	0.46	0.46
	Effluent	9.06	9.06	9.06
Total 2		17	27	24
Total 1+2		42	46	42

6. **Conclusions**

From this work we can conclude that:

The acid treatment technology is a very interesting and simple way in reducing the amount of chemicals to bleach the eucalyptus pulp. There are several opportunities in replacing bleaching chemicals with this stage, especially the expensive or bottlenecked chemicals. The steam consumption and the layout of the bleach plant are points of careful evaluation with respect to operating cost, installation and the payback of the investment.

There are several possibilities to design an acid stage according to each mill needs. The acid treatment does an important reduction of the chemicals consumption at a lower cost than other acid oxidants (ozone and peracids).

The observation that several eucalyptus pulps that are submitted to constant conditions present similar kappa reduction and distinct viscosity drop suggest that the reaction is not very selective. This supports the belief that given the adequate reaction kinetics, the hydrolysis occurs inespecifically in the ultra-structure of the fibers.

Appendixes (materials and methods)

The kappa numbers of the pulps have been defined according to standard ISO-302:1981, the viscosity according to standard ISO 5351-1:1981, and the brightness according to standard ISO 3688:1981.

The eucalyptus pulps are industrially washed samples from several mills, collected after the digester and after the oxygen delignification steps. Typical kappa numbers are 14-15 after the digester and 9-10 after delignification. The viscosities ranged 900-1300 cm^3/g according to the sampling point.

The conditions for the acid and bleaching stages are expressed in the Table below. The pulp consistency is 10%, except for the Z stage (40%). Chlorine dioxide charges are expressed as active chlorine.

	(A)	(D)	(Z)	(E)	(EO)	(EOP)
Time, min	10-300	10-180	1-5	10-60	60	60
Temperature, °C	90-130	50-80	ambient	80-85	80-90	80-90
charge, %	1-2	0.2-3.0	2.0-5.0	variable	3 kgf/cm^2	0.3-1.0
	H_2SO_4			NaOH	O_2	H_2O_2
pH	2-5	2-4.5	2-2.5	11	11	11

The one-stage acid treatment cited in the Table 7 with a pulp of kappa = 9.3 and viscosity = 900 cm^3/g, was performed at 98 °C; 300 min; pH =3.5. The final kappa = 4.5, viscosity = 790 cm^3/g and yield = 99%.

Literature cited

GELLERSTED, G., LINDFORS, E.-L. Hydrophylic groups in lignin after oxygen bleaching - TAPPI Journal, Atlanta, v.70, n.6, p-119-122, jun.1987.

RATNIEKS, E., SACON, V., ZIMMER, C., FOELKEL, C.E.B. A verdadeira eficiência da deslignificação por oxigênio. Guaíba, Riocell, 1994. 1p. Technical Report n.735. Paper presented to 1. Congresso Latino Americano de Deslignificação, ABTCP, 1994.

RATNIEKS, E., FOELKEL, C.E.B., SACON, V., ZIMMER, C. Stepwise survey on oxygen delignification an pulp washing performance. Guaíba, Riocell, 1995. 11p. Technical Report n.967. Paper presented to the TAPPI PULPING CONFERENCE, AIChE session, 1995.

SUN, Y-P.,NGUYEN, K.L., WALLIS, A.F.A. Totally chlorine-fre bleaching of eucalypt kraft pulp incorporating a UV-peroxide stage. Appita, Carlton, v.48, n.5, sept.1995.

VUORINEN, T., TELEMAN, A., FAGERSTRÖM, P., BÜCHERT, J., TENKANEN, M. Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. In: International Pulp Bleaching Conference, 1996, Washington. Proceedings...Atlanta, TAPPI. 646p. book 1, p.43-51.