Alternatives for Removing Extractives in the Manufacture of Total Chlorine Free Pre-hydrolysis Kraft Dissolving Pulp From *Eucalyptus citriodora*

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ABSTRACT

Alternatives for removing DCM soluble extractives in the production of high quality dissolving pulp from *Eucalyptus citriodora* wood were evaluated. The selected alternatives were intended to be easily adaptable to the pulping and bleaching processes chosen, namely pre-hydrolysis kraft pulping and TFC bleaching with the sequence OA(ZQ)P. They included (1) the incorporation of surfactants in all steps of pulp production, (2) brownstock refining at low intensity, and (3) partial removal of fines through pulp fractionation in a 200 mesh screen. Despite the significant yield shrinkage, the most efficient treatment for the removal of DCM soluble extractives was the taking off of fines through fractionation but this technique resulted in significant yield loss. On the other hand, pulp refining at low intensity allowed the production of high quality dissolving pulp with no significant yield loss. The use of surfactants alone, even at very high dosages, was inefficient to remove extractives in all steps of pulp production. The most suitable phase of the process to use surfactants is in the peroxide bleaching stage.

Keywords: Extractives, TCF Bleaching, Eucalyptus citriodora

INTRODUCTION

Dissolving pulps are usually used to manufacture cellulose derivatives such as esters (viscose, rayon, acetates, etc.) and ethers (methyl cellulose, carboxymethyl cellulose, etc). The quality requirements for dissolving pulps may vary significantly depending upon the type of derivative being made. The most important characteristics of a dissolving pulp are: (1) a high content of α-cellulose, (2) an homogeneous molecular weight distribution of the cellulose chains, (3) a low content of impurities such as degraded cellulose, hemicelluloses, lignin, inorganic compounds and **extractives**.

Dissolving pulps are special grades of cellulose pulp and are usually produced from cotton linter or wood. When manufactured from wood, the cooking processes used are usually the acid sulfite or the pre-hydrolysis kraft. The world production of cellulose derivatives requires 3.6 million tons of dissolving pulp, being 90-95% of this pulp manufactured from wood and the rest from cotton linter (HINCK et al.,1985).

According to KOGLER (1994), since the beginning of the century the world consumption of textile fibers has increased constantly, growing from 3.9 million tons in 1900 to 40.4 million tons in 1993. In this very same period, the world population increased from 1.6 to 5.5 billions which raised the *per capta* consumption from 2.5 to 7.3 kg.

The textile fibers may be classified into two groups according to their absorbing potential: (1) The absorbing group which includes cotton, wool, and processed cellulose fibers and (2) The non-absorbing group which includes the synthetic fibers (polyester, polypropylene and nylon). The production of synthetic fibers has increased continuously since mid 50's. However, there are certain characteristics of the absorbing fibers, which make them very attractive and may turn them very important in the near future. These include their biodegradability and the fact that they are produced from renewable raw materials. In Europe, and particularly in the USA, the viscose fibers are becoming a very important source of fibers for the textile industry. It is projected that in the year 2000 the demand of absorbing fibers will be of 28 million tons per year. Considering the existing limitations for the increase in the production of cotton (18.5 million tons) and wool (1.6 million tons), it is believed that the processed cellulose fibers (2.7 million tons) will assume an important position in this market in the future, even considering their high production costs which are mainly due to rigid environmental constraints.

Besides generating a product with rigid quality specifications, the dissolving pulp manufacturing process must use technologies of minimum environmental impact. These include total chlorine free bleaching and partially closed mill water cycles. These technologies are little effective in the removal of extractives from the pulp, particularly those of the neutral type unsaponifiable.

The objective of this work was the production of high quality dissolving pulp from *Eucalyptus citriodora*, using a total chorine free bleaching technology, with emphasis in the removal of extractives. To this goal, several alternatives to remove extractives, which are well adapted to the pre-hydrolysis kraft pulping process and to the OA(ZQ)P TCF bleaching sequence were evaluated. These included: (1) the incorporation of surfactants in all steps of pulp production, (2) brownstock refining at low intensity, and (3) partial removal of fines through pulp fractionation in a 200 mesh screen.

EXPERIMENTAL

Eucalyptus citriodora wood chips from northern Bahia, Brazil, were used. The wood chips were ground in a Wiley mill to produce sawdust for chemical analysis according to Tappi procedure T 257 om-85. The chemical analyses were effected on the 40/60 mesh fraction obtained after the sawdust fractionation.

The use of surfactants in the process was evaluated in the kraft cooking, in the refining of the brown pulp, in the oxygen delignification and in the peroxide bleaching stage, at the rate of 0.05% on the wood or pulp dry weight. In the kraft cooking, several surfactants compatible with an alkaline pH and their combinations were evaluated. Preliminary tests indicated that the mixture at the 1:1 ratio of the oleic and keto-stearic ethoxylated alcohol's were the most effective surfactant for alkaline conditions and was thus used throughout this work.

Pulp fractionation to remove fines was carried out with 10 g o.d. pulp samples on a laboratory scale system equipped with a 200 mesh stainless steel screen. The fractionated samples were washed thoroughly before determination of the DCM extractives.

Low intensity refining of the brownstock was carried out in a Jokro mill. The refining was carried out with 16 g o.d. of pulp at 6% consistency and 28 ± 0,5 °C and pH

9.5, during 15 min. The adjustment of pH to 9.5 was effected using black liquor from the cooking operation. Prior to the refining procedure, the pulp was soaked for two hours at this pH value. After refining the pulp was disintegrated in a blender at 3000 revolutions and 0.8% consistency for 15 and then homogenized for 10 min at 0.2% consistency. Following, the pulp suspension was collected in nylon bags and the yield and DCM extractable content determined.

The preparation of the dissolving pulp was carried out with the pre-hydrolysis kraft cooking process. The general conditions for the pre-hydrolysis and kraft cooking process are shown in Table 1. These conditions were adjusted so as to produce a pulp of 10-12 kappa, 1200 dm^3/kg viscosity and less than 3% solubles in NaOH 5%.

Table 1 - General conditions for pre-hydrolysis and kraft cooking

Conditions	Phases	
	Pre-hydrolysis	Kraft Cooking
Wood Chips, g	2300	1800
Active alkali, % as NaOH	---	20
Sulfidity, %	---	30
Liquor/wood ratio	3.5:1	4:1
Maximum temperature, ° C	170	160
Time at temperature, min	30	60
H Factor	410*	447**
Initial pH	5.5	---

* k = exp. [41,5 - 15,487/T]
** k = exp. [43,2 - 16,113/T]

The bleaching of the pulp was effected with the sequence OA(ZQ)P. The general bleaching conditions used in each stage of this sequence are shown in Table 2.

Table 2 - General Bleaching Conditions

	Bleaching Stage				
Conditions	O	A	(Z	Q)	P
Consistency, %	10	5	45	10	12
Temperature, ° C	90	60	room	60	80
Retention time, min	75	30	<1	30	300
O_2 charge, %	2	---	---	---	---
O_3 charge, %	---	---	0.35	---	---
H_2O_2 charge, %	---	---	---	---	0.8
NaOH charge, %	2.8	---	---	---	---
Initial pH	---	2.5	2.5	6.0	11.5
Mg, ppm	667	---	---	---	200
EDTA , %	---	---	---	0.2	---

The main pulp analysis including kappa and $KMnO_4$ numbers, brightness, viscosity, NaOH 5% solubility, α-cellulose content and DCM extractives were carried out according to Tappi standard procedures.

- RESULTS AND DISCUSSION

Physical-chemical Analysis of the Wood

The average physical-chemical characteristics of the *Eucalyptus citriodora* wood are shown in Table 3. In general, the values obtained for this wood are typical for the *Eucalyptus* genus, except for the contents of ash and of DCM extractives, which were very high. These attributes are negative for the production of dissolving pul. removed from the wood when it is treated with an extraction sequence comprising of ethanol, ethanol/toluene and hot water. These chemical compounds which are classified as secondary or stranger compounds are not a essential part of the cell wall (SJÖSTRÖM, 1981). This wood fraction includes compounds of low polarity such as waxes, fats, resin acids, sterols and non-volatile hydrocarbons, and compounds of higher polarity such as low molecular weight carbohydrates, mineral salts and other water soluble materials.

The DCM extractable compounds are usually comprised of the low polarity materials. According to the Tappi standard procedure, the ether extraction was replaced with the DCM one since the latter extracts the very same compounds extracted by the former with the advantage of being less flammable.

A significant fraction of the wood extractives are removed during alkaline cooking because they react with alkali. However, a large fraction of the DCM extractable ones may remain in the pulp after cooking giving rise to pitch problems in the pulp and mill equipment.

Table 3 - Physical-Chemical Characterization of *Eucalyptus citriodora* Wood

Characteristics	Results
Wood density, kg/m^3	586
Holocellulose, %	74.9
α-cellulose, %	45.7
Pentosans, %	17.8
Insoluble lignin, %	15.1
Soluble lignin, %	3.74
Total lignin, %	18.8
Total extractives, %	5.68
DCM extractives, %	0.62
Ash, %	0.62
Metals, ppm:	
Calcium	2.403
Magnesium	398
Iron	47.5
Manganese	6.11
Copper	1.53

Alternatives to Remove DCM Extractives

Three alternatives were evaluated to remove DCM extractives: (1) the incorporation of surfactants in various phases of the process, including cooking, washing under agitation after refining, oxygen delignification and peroxide bleaching; (2) brownstock refining at low intensity; and (3) partial removal of fines through pulp fractionation in a 200 mesh screen.

The percent removal of DCM extractives based on wood weight for the three different treatments are shown in Figure 1. The treatments were designed so as to avoid interaction between treatments. The true effect of each isolated treatment was measured. The results indicate that the use of surfactants in the alkaline cooking that follows acid pre-hydrolysis (PHK stage) is inefficient to remove DCM extractives. As seen in the upper part of the first bar, only 3.2% of the extractives removed in the PHK stage were in fact due to the surfactant.

Refining of the brownstock followed by washing under agitation resulted in removal of 24.2% DCM extractives. The addition of 0.05% surfactant during washing resulted in an extra 3.3% removal. The refining followed by washing under agitation is effective because the mechanical action of refining breaks parenchyma cells and release the extractives while the washing under agitation wash them out from the cells. The washing after refining likely had the effect of dissolving the saponifiable compounds while the unsaponifiable ones (3.3%) were removed with the help of surfactants.

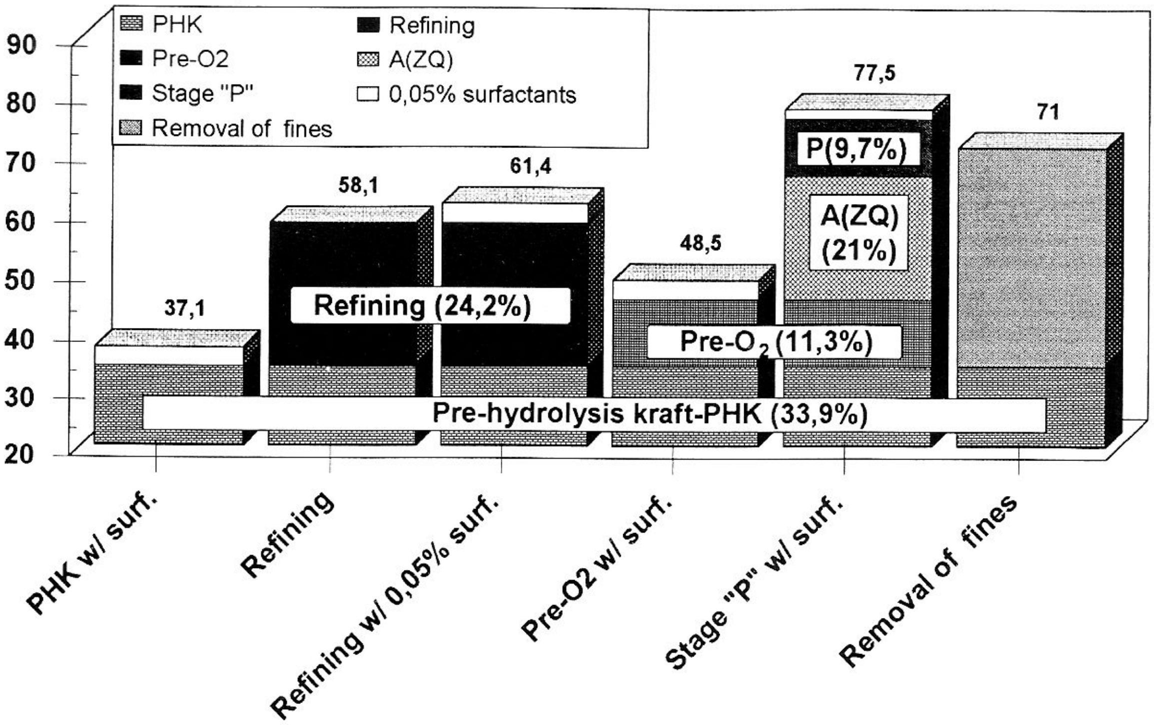
Efficiency of tretments, % wood

Figure 1- Effect of various treatments aimed at removing DCM extractives from *Eucalyptus citriodora* wood and pulp.

The most efficient technique to remove DCM extractives was the removal o pulp fines through brownstock fractionation in a 200 mesh screen. As shown in the last column of Figure 1, this treatment removed 37.1% of the extractives, which in addition to the 33.9% removed during the pre-hydrolysis kraft cooking (PHK) resulted in a total of 71.0%. This can be explained by the removal of fines, which comprised mostly of parenchyma cells and fiber fragments. The large majority of the

DCM extractives present in the wood are located in the parenchyma cells as shown in Table 4.

Table 4 - Average results of the *Eucalyptus citriodora* brownstock fractionation

Fiber fractionation in 200 mesh screen	
Fractions	DCM extractives (% pulp wt.)
Brownstock	0.98
Coarse fraction	0.49
Fine fraction [a]	10.4

[a] Fine fraction represented 9.4% of total brownstock weight.

The extractive removal techniques must suit the dissolving pulp production process. For instance, the refining treatment is a viable alternative in the industrial scale because it is easily adaptable to the whole process, specially if performed prior to the oxygen delignification. However, a washing step after this treatment may be questionable on the grounds of the high investment required to install a washer. For this reason, in the laboratory simulations, the pulp was only thickened after refining and not washed. Part of the filtrate obtained after pulp thickening was used for consistency adjustments in the oxygen delignification. Additionally, the use of pulp refining prior the oxygen delignification is advantageous because it reduces the amount of extractives going into the bleach plant since these compounds return to the recovery system with the filtrates of the oxygen delignification.

The most interesting place to add surfactants in the whole process is in the peroxide bleaching stage. The easiness of extractives removal decreases when approaching the end of the bleaching process. Thus, the extractives still remaining in the pulp before the P-stage, which are mostly unsaponifiable compounds that resisted to all types of pulp washing, may be emulsified by the surfactants and removed in the last washing stage. The P-stage conditions are quite adequate for the use of surfactants because of the high pH, high temperature and long retention time used in this stage.

The results above discussed lead to the conclusion that the most suitable combination of alternatives to remove extractives from the *Eucalyptus citriodora* pulp are the refining of the pulp at low intensity followed by the addition of 0.05% of surfactants in the P-stage of the sequence OA(ZQ)P. This combination of treatments was used in the production of dissolving pulp which will be discussed in the following section.

The Manufacture of Dissolving Pulp from *Eucalyptus citriodora*

The characteristics of the *Eucalyptus citriodora* pulp throughout the manufacturing process are shown in Table 5. The pulp was characterized after the pre-hydrolysis kraft cooking (PHK), after the oxygen delignification (O-stage), after the A(ZQ) bleaching stage and after the peroxide bleaching stage (P). This characterization was carried out on untreated samples (conv.), on samples that were refined to remove extractives (ref.) and on samples that were refined and further treated with surfactants in the P-stage (ref. + surf.). The emulsification treatment was carried out with 0.05% of a surfactant mixture comprised of a 1:1 ratio of oleic and keto-stearic ethoxylated alcohols.

As expected, the yield of the pre-hydrolysis kraft cooking process reflects the wood chemical composition. The yield value of about 42% is close to the wood α-cellulose content (Table 1). On the other hand, the yield of the acid pre-hydrolysis in itself was 80.2%, a value close to the content of pentosans in the wood (Table 1). The oxygen delignification yield was about 97%, indicating that this stage is a very selective one. During the oxygen treatment, the reducing end groups of the carbohydrates are oxidized to carboxylic acids (GRATZL, 1990), thus preventing yield loss in this stage through alkali promoted peeling of cellulose chains, which can occur in temperatures in the range of 60-150 °C (Rydholm, cited by GOMIDE, 1979).

The peroxide bleaching stage yield was in the range of 95%, being a little lower than those of the other bleaching stages. However, the overall yield loss based on wood weight during the A(ZQ)P bleaching was in the range of 4%, which can be considered low. The total process yield including pulping and bleaching was about 40%, which is typical for hardwood dissolving pulps. It should be mentioned that this number is not very far of the content α-cellulose originally present in the *Eucalyptus citriodora* wood.

Table 5- Average characteristics of the *Eucalyptus citriodora* dissolving pulp throughout the manufacturing process, including pre-hydrolysis kraft pulping and OA(ZQ)P TCF bleaching

Treatments		Total yield (%)	Kappa or $KMnO_4$ No.	Bright., (% ISO)	$[\eta]^a$ (cm^3/g)	S_5 [b] (%)	α-cellulose (%)	DCM extractives [c] (% pulp)	Total removal [d] (% wood)
PHK	Conv	42.6	10.4*	35.0	1292	3.05	---	0.99	32.0
	Ref.	41.8	---	33.9	1238	2.69	---	0.63	25.6
After O-stage	Conv.	41.7	4.0*	57.8	1006	---	---	0.50	34.4
	Ref.	40.8	4.0*	53.1	622	---	---	0.29	49.0
After A(ZQ)	Conv.	41.3	0.4**	80.8	684	---	---	0.36	9.61
	Ref.	40.6	0.3**	77.3	485	---	---	0.22	4.69
After A(ZQ)P	Conv.	40.0	0.3**	88.1	508	2.22	95.2	0.31	4.0
	Ref.	38.9	0.4**	87.3	385	2.28	94.4	0.18	3.1
	Ref. + surf.	38.7	0.3**	89.5	382	2.18	94.3	0.15	5.0

[a] Intrinsic viscosity

[b] Pulp soluble in NaOH 5%

[c] Extractives soluble in DCM

[d] DCM extractives removal based on the original content of these extractives on wood (0.62%).

*Kappa number

**$KMnO_4$ number

The charge of ozone applied (0.35%) in the Z-stage of the OA(ZQ)P sequence was decided based on the pulp kappa number after the O-stage. The goal was to reach an almost complete lignin removal in the Z-stage so as to meet the less than 0.1% lignin content in the final bleached pulp which has been specified for dissolving pulps (FOELKEL et al., 1978). The values of residual lignin ($KMnO_4$ Nº) shown in Table 5 ratifies the well known ozone efficiency as a delignifying agent. However, the lignin removal was achieved at the expense of substantial viscosity losses. The attack of the ozone on the cellulose chains was probably intensified because of the low contents of lignin and hemicelluloses existing in the pulp prior to this stage (SIXTA et al., 1994).

For the production of dissolving pulp, the intense cellulose degradation has a negative effect because it decreases the pulp α-cellulose content. However, in all cases the final values of α-cellulose reported in Table 5 are within the market specifications for most applications of dissolving pulps.

The values of pulp solubility in NaOH 5% were only slightly affected by the TCF bleaching operation. This indicates that only a small fraction of the low molecular weight material not extracted during the pre-hydrolysis kraft cooking is removed during bleaching. The small losses in the bleaching occurred likely through the removal of certain xylans which were linked to the residual lignin - lignin-carbohydrate complexes, through alkali induced peeling reactions of hemicelluloses and through alkaline dissolution of low molecular weight hemicelluloses which may have been cleaved by the oxidative action of ozone and its free radical derivatives.

The viscosity drop during bleaching was more intense in the case of the refined (ref.) pulp samples because there occurred a copper contamination of the pulp during refining caused by erosion of the Jokro mill refining elements. Purportedly, copper ions are very effective catalysts for organic and inorganic peroxides via free radical chain reactions (COLODETTE e DENCE, 1989), giving rise to hydroxyl ($HO^{\cdot}$) and other powerful radicals. In the case of the refined pulps, which picked up copper from the Jokro mill refining bars, the negative effect of the copper on pulp viscosity showed up immediately after the O-stage where significant amounts of organic ($ROO^{\cdot}$) and inorganic ($HOO^{\cdot}$) peroxides were generated. These peroxides gave rise to highly reactive radicals which cause cellulose degradation (GRATZL, 1990). The negative effect of the copper on pulp viscosity during O-stage has also been reported in other studies (COLODETTE et al, 1990).

During peroxide bleaching, there was no significant change in the pulp lignin content as measured by the $KMnO_4$ number but the pulp brightness increased substantially, up to 12 points, and the viscosity dropped. The viscosity shrinkage at this stage may be related to the previous ozone stage, which purportedly generates significant amount of carbonyl groups in pulp carbohydrates. These groups are the main responsible for viscosity and yield losses besides causing pulp brightness reversion in subsequent alkaline stages GRATZL (1990).

The content of DCM extractives measured in the pre-hydrolysis kraft pulp, based on wood weight, was higher then in the original pulp. This occurred because of the removal of wood constituents such as lignin and hemicelluloses in this stage of the process, which proportionally increased the fraction of DCM extractives in the pulp. The oxygen delignification was effective to remove DCM extractives (c.a. 49%) with the advantage that the extractives removed in this stage can be are burned in the recovery system, thus getting out of the system

The low intensity refining of the pulp in the Jokro mill resulted in significant decrease oh the pulp DCM extractive content, indicating that this treatment is efficient to break the parenchyma cells, thus increasing the accessibility of the extractives to DCM.

The significant removal of DCM extractives by the combination of pulp refining followed by oxygen delignification indicates that a significant fraction of the extractives found in the brownstock are soaped in alkaline media. This result confirm also the fact that the physical restrictions imposed by the parenchyma cell walls are the major reason for the difficulty to remove extractives during the pre-hydrolysis kraft pulping. As shown in Table 4, most of the DCM extractives are located in the parenchyma cells.

The *Eucalyptus citriodora* showed a good potential to produce dissolving pulp. The only negative aspect of the pulp was the higher than desirable content of DCM extractives in the bleached pulp (0.31%). A limit of less than 0.2% based on pulp weight is usually suggested. However, if the brownstock is submitted to light refining prior to the oxygen delignification, the DCM extractives content in the pulp can be decreased to acceptable levels (0.18%). Furthermore, if a combination of refining and the use of surfactants in the peroxide bleaching stage are applied the DCM extractives content decreases to values in the range 0.15%. Being an alkaline stage, the peroxide bleaching was somewhat ineffective to remove DCM extractives, indicating that residual extractives in the pulp are mostly neutral or unsaponifiable_compounds.

CONCLUSIONS

The results discussed above showed that the production of TCF bleached dissolving pulp grade from *Eucalyptus citriodora* is viable and also lead to the following major conclusions:

Although of difficult implementation, the most effective alternative to remove extractives from the pulp is pulp fractionation to remove fines.

The refining of the pulp at low intensity prior to the oxygen delignification showed to be the most viable alternative to remove pulp extractives in an industrial scale.

When required, the use of surfactants in the process should be effected in the peroxide bleaching stage, as a complement to other extractive removing techniques. The use of surfactants alone in any stage of the process is not a viable alternative to remove pulp extractives.

The fine fraction (200 mesh) of the *Eucalyptus citriodora* dissolving pulp contains most of its DCM extractives

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