Mixed Brazilian Eucalyptus and Pinus Species - Bleaching Evaluation

Ana Gabriela Monnerat Carvalho Bassa
Marcelo Rodrigues da Silva
Alexandre Bassa
Vera Maria Sacon
Votorantim Celulose e Papel
Research & Development
Jacareí – São Paulo – Brazil
Contact: gabriela.monnerat@vcp.com.br

Flavia Schmidt
Francides Gomes da Silva

Universidade de São Paulo
Agriculture and Forest School
Piracicaba – São Paulo – Brazil

Abstract

Eucalyptus fiber is shorter in relation to softwood species. These short fibers are useful in improving paper formation, but strength properties are better when long fibers are used. Most Brazilian pulp production uses eucalyptus species as raw material. Pulp production from softwood is concentrated in the south of Brazil due to the suitability of its climate for growing pine species. Looking for the possibility of obtaining pulp with adequate properties for formation and strength, this paper analyzes results of kraft pulp bleaching by the (OO)(AD)EopDP bleaching sequence, using pulps produced with mixtures of *Eucalyptus grandis* x *Eucalyptus urophylla* hybrid and *Pinus taeda* wood chips, and *Eucalyptus globulus* and *Pinus taeda* wood chips. Target brightness was 88.5 ± 1 % ISO. Chlorine dioxide consumption of the *Eucalyptus* tested was around 10 kg ClO_2/odt. For the mixtures of eucalyptus and pine in the proportions of 10% up to 50% pine, it varied from 11.2 up to 16.2 kg ClO_2/odt, increasing as the proportion of pine wood chips increased in the mixtures. Hydrogen peroxide consumption varied from 5 to 8 kg H_2O_2/odt for the pulps analyzed. Total active chlorine consumption for *Eucalyptus globulus* was 40.4 kg/odt, while for the *Eucalyptus grandis* x *Eucalyptus urophylla* hybrid it was 41.1 kg/odt. In the mixtures it varied from 41.9 up to 64.5 kg/odt, the consumption of the mixture of the *Eucalyptus grandis* x *Eucalyptus urophylla* hybrid and *Pinus taeda* being higher. For *Pinus taeda*, active chlorine consumption was 76.5 kg/odt. Viscosity values had a tendency to decrease as the proportion of pine increased in the mixtures. Brightness reversion varied from 1.7% to 2.5% ISO in the mixtures. In conclusion, manufacturing units that want to produce a differentiated kind of pulp with a high resistance to tearing, to get higher productivity from paper machines, or even to produce special, low-gram papers, must consider the addition of small proportions of *Pinus* to *Eucalyptus*.

1. Introduction

The main raw material sources for pulp and paper production in Brazil come from reforestation of the genera *Pinus* and *Eucalyptus,* with the main comparative advantages in Brazil being the development of eucalyptus-based short-fiber pulp and its success on the international market.

Eucalyptus grandis x *Eucalyptus urophylla* hybrids are prominent in Brazilian forestry because of their rapid growth, with felling cycles of between six and seven years of age, and their good performance in the production of pulp and paper. Technological advances in the forestry area and in the selection of superior populations, families, and individuals have achieved a high wood production level of around 40 to 50 m^3/ha/year, allied to good wood properties, with pulp yields of between 50% and 54% and wood density of around 0.500 to 0.520g/cm^3.

Pinus plantations in Brazil evidence volumetric growth of between 20 and 30 m^3/ha/year, and rotation is about 20 years, with plantations being thinned out at 8 and 14 years of age. Wood at 8 and 14 years of age is used for pulp and paper production and the wood from the final felling, at 20 years of age, is used in sawmills and lamination. The pulp yield from *Pinus,* when wanting to produce bleached papers, is low - between 40% and 45%, and its wood density, depending on age, can reach from 0.300 to 0.400g/cm^3.

When comparing these two genera, or even within the same genus, we noted marked differences, amongst them the length of the fibers. The fibers from the genus *Eucalyptus* present a length of between 0.5m and 1.5 mm. *Pinus,* in turn, presents long fibers (measuring between 3mm and 6mm in length) and consequently produces papers with high physical-mechanical resistance which, besides providing the paper with specific characteristics, allows higher paper machine speed due to the greater resistance of wet and dry sheets, and easier drainage. Greater wet and dry sheet resistance and ease of drainage can mean greater efficiency in paper production, and lower production costs.

Foelkel reports some advantages of hardwood pulps, such as: better sheet formation; better surface properties, good mechanical properties, lower flow resistance, lower lignin level in the wood, and a higher level of hemicelluloses. The hardwood's disadvantages for cellulose production have been listed as: lower resistance to tearing, lower wet sheet resistance, and the presence of vessels, which can be harmful as fragments may rise up from the surface of the paper during printing (1).

Chen and coworkers have stated that there are few published studies on cooking mixtures of short and long fiber wood and they showed that the addition of *Populus tremuloides* woodchips to *Picea glauca* woodchips for kraft pulp production resulted in a rise in screened yield of between 2% to 4%, lower generation of rejects, little effect on alkali consumption, and better delignification (2).

Oliveira and coworkers studied the production of kraft pulp using conventional cooking based on mixtures of *Pinus strobus* var. *chiapensis* woodchips and *Eucalyptus urophylla* woodchips of a hybrid origin in proportions of 33%, 66% and 100% *Pinus strobus*. The results showed that as the level of *Pinus strobus* wood increased in the mixture, the screened yield fell markedly. An increase in the proportion of *Pinus strobus* woodchips led to an increase in the kappa number. As regards the physical-mechanical properties, the percentage of *Pinus* woodchips in the mixture had a significant effect on the refining process, with a greater energy consumption being required (3).

The differentiated qualities of the wood commented on previously impact the pulp production process and the characteristics of the final product, which depends on the quality of the wood and the fabrication process conditions.

Modern eucalyptus kraft pulp bleach plants are usually equipped with: (1) single (O) or double (O/O) oxygen delignification; (2) a first bleaching stage comprised of a conventional chlorine dioxide stage (D_0) or hot chlorine dioxide bleaching at high temperature (D_{HT}) or a sequential treatment with hot acid hydrolysis and chlorine dioxide (A/D) or a sequential treatment with ozone and alkali (Z/E) or a sequential treatment with ozone and chlorine dioxide (Z/D); (3) a second bleaching stage comprised of oxidative extraction with hydrogen peroxide (EP), oxidative extraction with oxygen and peroxide (EPO) or peroxide pressurized extraction (PO); a third bleaching stage with one chlorine dioxide reactor (D_1) or with two reactors, without inter-stage washing (DN/D) ; (5) a fourth bleaching stage with chlorine dioxide (D_2) or hydrogen peroxide (P). The fourth stage is optional and required only when brightness of 92%ISO are needed. There are some variations of these basic strategies, but the large majority of the pulp mills that bleach eucalyptus use them (4).

This study analyzes the results of kraft pulp bleaching by the (OO)(AD)EopDP bleaching sequence, using pulps produced with mixtures of *Eucalyptus grandis* x *Eucalyptus urophylla* hybrid and *Pinus taeda* wood chips and *Eucalyptus globulus* and *Pinus taeda* wood chips.

2. Materials and Methods

2.1 Materials

Three wood species used in this study were:

- Hybrid of *Eucalyptus grandis x Eucalyptus urophylla* at 7 years old, from the Votorantim Celulose e Papel (VCP) commercial forest;
- *Eucalyptus globulus* of 7 years old from a trial set at Aracruz Guaíba;
- *Pinus taeda* of 9 years old from the Klabin commercial forest.

The chips from each source were produced separately. After chipping, the samples were mixed in the proportion of 10% to 50% of *Pinus taeda* with the eucalyptus samples. The proportions used for pulping are described in the Table I.

Table I – Material Description for Cooking

Eucalyptus grandis x Eucalyptus urophylla	*Pinus taeda*	*E. globulus*	*Pinus taeda*
100%	0%	100%	0%
90%	10%	90%	10%
80%	20%	80%	20%
70%	30%	70%	30%
60%	40%	60%	40%
50%	50%	50%	50%
0%	100%	0%	100%

The pulps were produced by Lo-solids® cooking simulations. In Table II the characterization of brownstock pulps are presented. The kappa target number in the cooking was 18 ± 1 for *Eucalyptus* species and 26 ± 1 for *Pinus taeda*. For the wood mix cooking, looking to preserve the yield, the kappa number target was increased in proportion to the amount of pine content.

Table II – Characterization of Brownstock Pulps

Eucalyptus grandis x Eucalyptus urophylla + Pinus taeda	Kappa Number	Lignin content (%)	HexA. mmol/kg	Viscosity. cP	Brightness. %ISO
0% Pinus	17.9	3.47	50.41	93.2	49.2
10% Pinus	19.1	2.56	56.06	46.0	50.7
20% Pinus	19.0	3.02	51.25	36.0	47.6
30% Pinus	20.3	2.70	39.57	35.1	43.9
40% Pinus	21.0	3.78	40.97	30.1	43.6
50% Pinus	22.1	3.93	43.49	32.5	36.9
100% Pinus	25.6	3.59	30.35	26.4	33.5
E. globulus.+ Pinus taeda	**Kappa Number**	**Lignin content (%)**	**HexA. mmol/kg**	**Viscosity. cP**	**Brightness. %ISO**
0% Pinus	17.2	2.73	50.50	82.8	52.9
10% Pinus	17.9	3.88	56.59	43.3	51.8
20% Pinus	19.3	3.56	55.68	35.4	50.1
30% Pinus	20.7	3.28	50.03	34.5	45.4
40% Pinus	21.2	3.75	47.76	35.0	44.3
50% Pinus	22.1	3.54	42.62	33.7	42.3
100% Pinus	25.6	3.59	30.35	26.4	33.5

2.2. Methods

The general bleaching conditions and the methods used are shown in the Table III and IV, respectively.

Double stage oxygen delignification (O/O) and pressurized peroxide bleaching (EPO) were performed with 250-280 g oven dried pulp samples in a Teflon-lined mixer/reactor (Quantum Technologies, model Mark V). The charges of chemicals were added to the reactor after the desired pulp temperature was reached, and the reaction pressure was adjusted with oxygen when necessary. After the pre-established reaction time elapsed, the reactor pressure was released, the pulp was discharged into a 150 mesh screening box and 300 ml of liquor were squeezed from the pulp for analysis.

Chlorine dioxide (D), hydrogen peroxide (P) and acid (A) bleaching stages were performed in polyethylene bags. In all cases, the required amounts of water and reagents were mixed with the pulp at room temperature and the samples were than placed in a heating bath for the desired reaction time. All bleaching stages were carried out in duplicate and inter-stage washing was carried out thoroughly.

Charges of bleaching agents were adjusted to reach the target brightness of 88.5 ± 1 % ISO.

Table III – General Bleaching Conditions

Conditions	Bleaching Stages					
	O/O	**A/**	**D**	**(EPO)**	**D**	**P**
Consistency, %	12	12	12	10	10	10
Time, min	15/45	120	13	65	120	120
Temperature, ^{0}C	95/105	90	85	85	75	80
Pressure, KPa	600/450	-	-	4,13	-	-
Final pH	11.0	3.0	2.5	11.0	4.5	11.0
Caustic, kg/odt	20/0	-	-	-	-	-
Oxygen, kg/odt	15/7	-	-	80	-	-
Kappa Factor	-	-	0.18/0.20	-	-	-
Chlorine Dioxide as Cl_2 , kg/odt	-	-	17.8-26.8	-	8.0	-
Hydrogen Peroxide, kg/odt	-	-	-	4.0-8.0	-	3.0-12.0

Table IV - Methods

Parameters	**Norms**
Kappa Number	TAPPI – T236 cm-85
Viscosity	TAPPI – T230 om-94
Brightness	ISO 2469-1980; ISO 2470-1977; ISO 3688-1980.
Brightness reversion	TAPPI-UM 200
Hexenuronic acids	Chai et al. (2001)

3. Results and Discussion

3.1 Oxygen Delignification

The use of oxygen-derived compounds, including ozone and hydrogen peroxide, in bleaching kraft pulp is rapidly increasing and the trend is for such reagents to dominate bleaching plants in the future. Oxygen, due to its low cost and high efficiency, will be used increasingly in carious stages of ECF and TCF bleaching, such as in single (O) or double (OO) pre-delignification (pre-O_2), oxidative extraction with oxygen (Eo) and/or hydrogen peroxide (Eop) and bleaching with pressurized peroxide (PO) (5).

The delignification stage with oxygen is used between pulping and bleaching. Chemically the oxygen acts preferably in phenolic structures free of lignin, causing their fragmentation, resulting thus in more soluble structures which are easier to remove (6).

Salvador et al., (7) state that in pre-bleaching, oxygen also works as an agent of delignification and bleaching, with delignification being limited to a reduction in the kappa by 30-40% for short-fiber pulps and 40-50% for long-fiber pulps.

The low selectivity of the oxygen and the difficulty in transference of efficient mass between the gaseous phase and the solid phase has limited the degree of delignification in softwood pulps to 45-55% in a single stage and the degree of delignification in hardwood pulp to 30-35%. However, the use of two sequential stages allows an increase in the degree of delignification, although much of this occurs in the first stage. Currently there are pulp mills using a double oxygen stage, for softwood and hardwoods pulps, achieving delignification of 65-75% in the case of softwoods (8).

Owing to the difference in efficiency in the pre-delignification stage with oxygen between pulp produced from long and short fibers, one hypothesis tested in this study is that after this stage kappa numbers for all the pulp evaluated in this study would level out. This is due to the difference in composition between the pulps, which in the case of *Pinus taeda*, presents a higher level of lignin and a lower level of hexenuronic acids, in addition to a higher kappa number for the pulp at the entry of pre-delignification with oxygen, characteristics which result in greater efficiency compared with eucalyptus cellulose pulps, which in turn have lower levels of lignin, higher levels of hexenuronic acids and lower kappa numbers after pulping. Hence, *Pinus taeda* pulp can be delignified in the pulping process, at higher kappa numbers, in order to preserve the pulp yield, supposing that in the pre-delignification stage with oxygen the three pulps evaluated separately and it's mixtures would have equivalent kappa numbers. The results obtained can be seen in table V.

Table V – Oxygen Delignification Stage Results

Treatment	***Eucalyptus grandis x Eucalyptus urophylla***	***Eucalyptus globulus***	***Pinus taeda***
pH final	11.5	11.0	11.0
Kappa number	10.3	10.9	14.1
Viscosity cP	76.6	73.1	22.8
Brightness (% ISO)	49.2	52.9	33.5
Efficiency of pre-O_2 (%)	42.4	36.7	44.9
Selectivity cP	2.3	1.5	0.3
Corrected kappa number	6.1	6.6	11.5

Figure 1 shows the results of the efficiency of pre-delignification with oxygen for the mixtures evaluated.

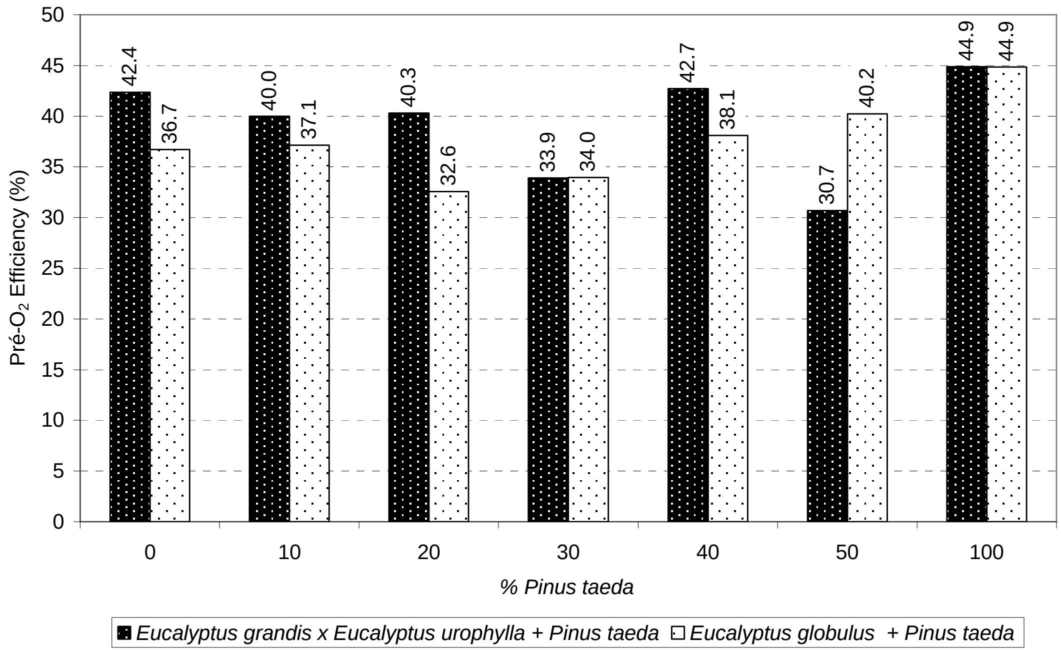


Figure 1. Oxygen Delignification efficiency.

Table V and figure1 show greater efficiency in the pre-O_2 stage for pulp produced from *Pinus taeda*. However, the pulp produced from *Eucalyptus grandis* x *Eucalyptus urophylla* presented similar efficiency to that obtained for the pulp produced from *Pinus taeda*, whilst for the pulp produced from *Eucalyptus globulus* efficiency of the pre-O_2 stage was lower. The levels of lignin in the pulps from the materials in question could explain the results obtained. It should be stressed that the conditions for delignification with oxygen were equal for all the pulps.

One fact of relevance is that pulps from long fiber require slightly stronger oxygen and alkali conditions in pre-O_2 which, allied to the higher kappa number at the entry of pre-O_2 and the higher lignin level in the pulp result in greater efficiency in the delignification and consequently lower kappa numbers. That is, if the conditions used in pre-O_2 for pulp from *Pinus taeda* had been more severe in terms of alkaline charge and oxygen load, the hypothesis of the study would have been confirmed for all the pulps evaluated. The kappa number from the mixtures of the species after the pre-O_2 stage can be seen in figure 2.

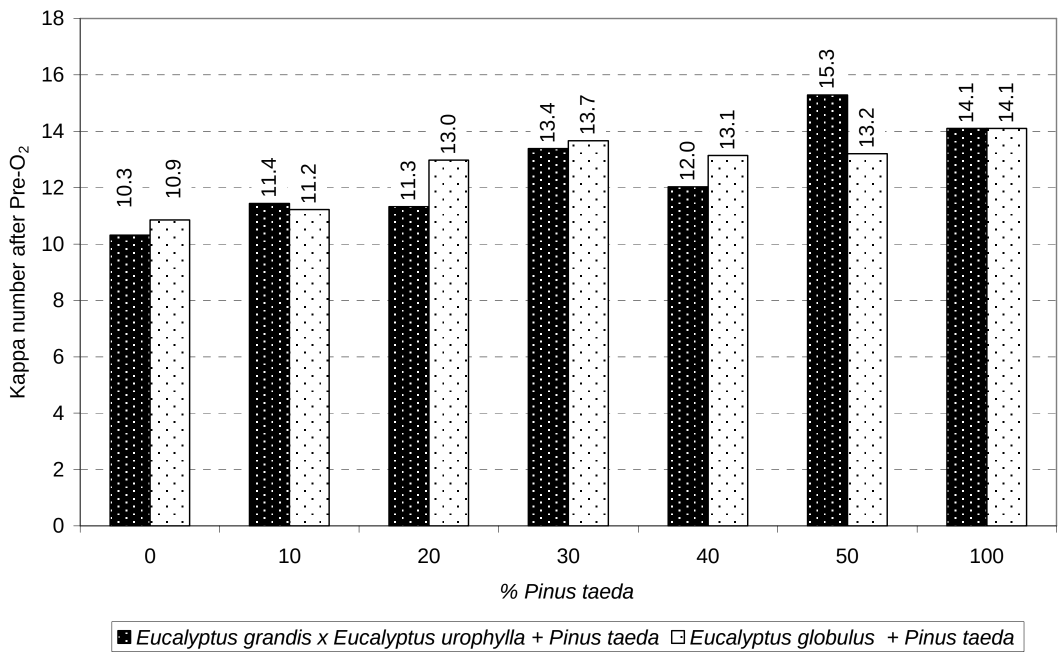


Figure 2 – Kappa number after Pre-O_2.

The brightness of the pulp from *Eucalyptus globulus*, at 52.86 % ISO stands out from the rest, indicating that this material is easier to bleach.

Greater selectivity is seen for pulp from *Pinus taeda*. This fact is due to the greater efficiency of the pre-O_2 stage combined with the low reduction of viscosity. The efficiency for pulps from *Eucalyptus* was lower, reaching 2.19 mPa.s for pulp from *Eucalyptus grandis* x *Eucalyptus urophylla*.

For kappa number correction (according to the level of hexenuronic acid content), at this stage a higher lignin level is seen in pulp from *Pinus taeda* (corrected kappa number of 11.5), whilst the pulps from *Eucalyptus* present corrected kappa numbers of 6.1 and 6.6.

3.2 Bleaching

The results of the bleaching analysis for brightness 88.5 ± 1 % ISO can be seen in tables VI and VII.

Table VI - Results of the bleaching analysis for *Pinus taeda* + *E. grandis* x *E. urophylla* mixtures

	E. grandis x E. urophylla	**% of *Pinus taeda* + *E. grandis x E. urophylla***					***Pinus taeda***
		10	**20**	**30**	**40**	**50**	
Pre-O_2 kappa	10.35	10.7	11.3	11.8	11.7	15	13.4
Eop kappa	1.7	2.9	1.7	2.8	2.3	1.6	2.2
Brightness. % ISO	88.9	88.6	88.2	87.5	87.6	88.3	87.7
Dioxide consumption (ClO_2. kg/odt)	10.1	11.2	11.6	13.5	13.4	18.2	13.2
Peroxide consumption (H_2O_2. kg/odt)	7	6	6	7	7	8	20
Chlorine dioxide consumption (kg/odt)	14.2	12.2	12.2	18.3	18.3	26.4	33.0
Final viscosity (g/cm^3)	18	15	12	12	13	14	9
Brightness reversion % ISO	3.4	2.3	2.0	2.2	2.5	2.4	2.1
CAT (Cl_2. Kg/odt)	41.1	41.9	43.1	50.1	49.9	64.5	76.5
Pre-O_2 Bleachability	4.0	3.9	3.8	4.2	4.3	4.3	5.7
Kappa factor	0.18	0.20	0.20	0.20	0.20	0.20	0.20

Table VII - Results of bleaching analysis for *Pinus taeda* + *E. globulus* mixtures

	E. globulus	**% de *Pinus taeda* + *E. globulus***					***Pinus taeda***
		10	20	30	40	50	
Pre-O_2 kappa	9.98	11.1	11.4	13.3	12.4	12	13.4
Eop kappa	1.6	3.1	2.7	2.3	2.4	1.7	2.2
Brightness. % ISO	89.2	88.8	89.1	89.2	88.4	89.5	87.7
Dioxide consumption (ClO_2. kg/odt)	9.8	11.5	11.7	11.7	14.0	16.2	13.2
Peroxide consumption (H_2O_2. kg/odt)	7	6	5	6	7	8	20
Chlorine dioxide consumption (kg/odt)	14.2	12.2	10.1	12.2	18.3	26.4	33.0
Final viscosity (g/cm^3)	27	17	18	18	14	14	9
Brightness reversion % ISO	2.7	1.7	2.0	2	1.8	1.8	2.1
CAT (Cl_2. Kg/odt)	40.4	42.7	41.2	43.3	51.4	59.3	76.5
Pre-O_2 Bleachability	4.0	3.8	3.6	3.3	4.1	4.8	5.7
Kappa factor	0.18	0.20	0.20	0.20	0.20	0.20	0.20

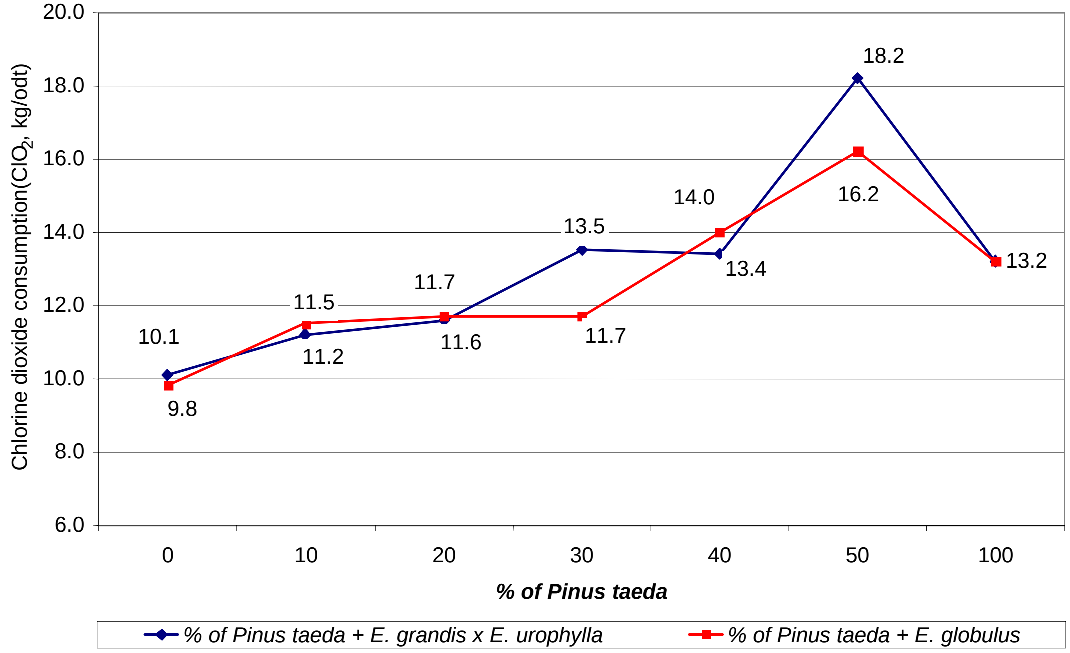


Figure 3 – Chlorine dioxide consumption.

For the chlorine dioxide consumption parameter, a certain similarity is seen between *Eucalyptus* and its mixtures with *Pinus taeda*, the greater the proportion of *Pinus taeda* in the mixture, the greater the consumption.. This was expected because the kappa number increase for pulps with a greater proportion of *Pinus* in the mixtures.

In the mixtures of between 30% to 40% *Pinus taeda* with *Eucalyptus*, the level for chlorine dioxide consumption in the 100% *Pinus taeda* treatment is achieved, indicating that from this proportion the consumption of chemicals in bleaching could be a limiting factor for the production of pulps from mixtures of *Eucalyptus* and *Pinus*.

For the 50% *Pinus* proportion in *Eucalyptus*, greater chlorine dioxide consumption than for 100% *Pinus* is seen. This result highlights that optimization studies as regards the sequence of bleaching and consumption of chemicals are necessary in order to obtain better results for the mixtures tested.

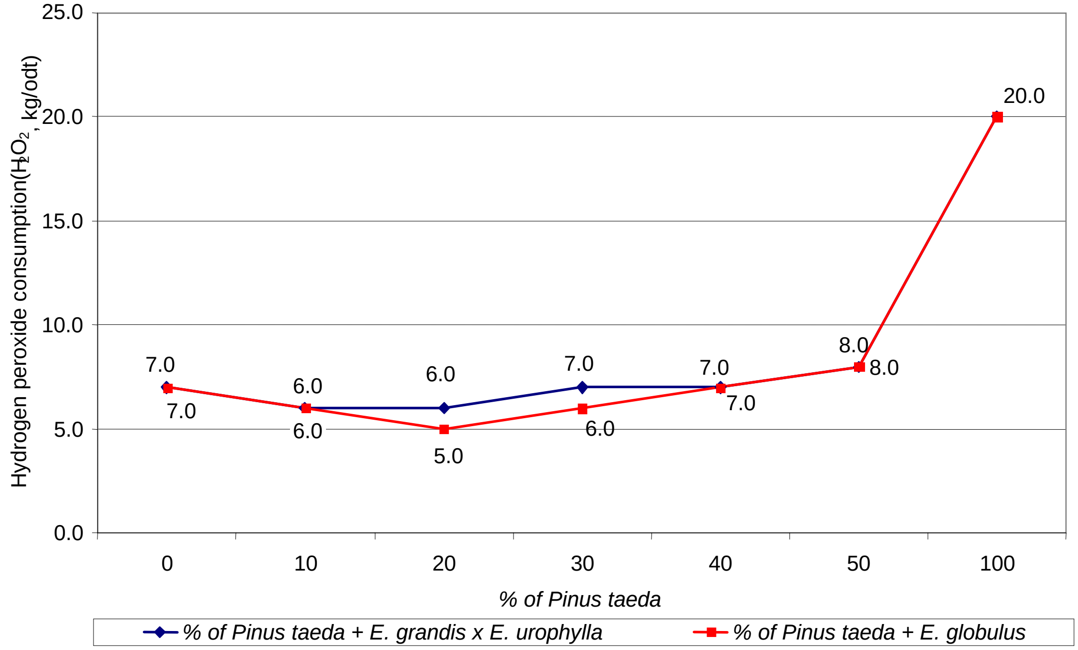


Figure 4 – Consumption of hydrogen peroxide.

With regard to consumption of hydrogen peroxide, certain stability is noted for the 100% *Eucalyptus* treatments and the mixtures of *Eucalyptus* and *Pinus*, with values varying between 5 to 8 Kg H_2O_2/odt. For the 100% *Pinus* treatment, however, a higher value of hydrogen peroxide is necessary to achieve brightness of 88 ± 1.

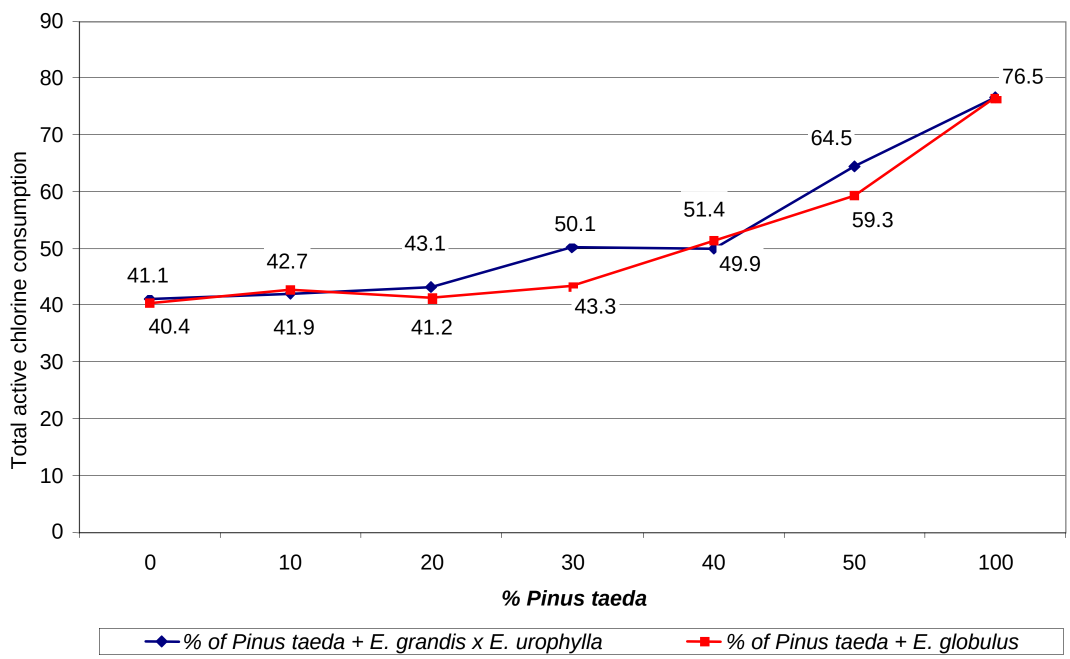


Figure 5 –Total active chlorine consumption.

Upon observing the consumption of TAC obtained for the 100% fractions *Eucalyptus* and *Pinus taeda*, a significant difference is noted for the different species of wood. This was expected because of the higher level of lignin in the *Pinus taeda* (9) and the need to preserve its yield. Pulps with a higher level of residual lignin (higher kappa number) need a greater quantity of bleaching reagents to achieve the brightness desired.

In addition, there is a strong influence of the hexenuronic acids formed in the cooking, eucalyptus having greater intensity. Hexenuronic acids contribute significantly to the pulp's kappa number. Li and Gellerstedt (10) state that the kappa number is equivalent to 11.9mmol of hexenuronic acids. Hence, the corrected kappa number can be calculated for the pulps. Thus, pulp from *Pinus taeda* would have a corrected kappa number of 23.05 compared to 13.66 and 12.96 for eucalyptus pulps.

The acid hydrolysis (A) stage markedly reduces these acid groups, which significantly minimizes the chlorine dioxide consumption for eucalyptus pulps. However, A/D technology is not recommended for *Pinus* pulps because they have a reduced level of hexenuronic acids and high lignin levels. The high temperature in acid condition condenses lignin and darkens the pulp. Nevertheless, as the focus purpose of this study is the mixture of small proportions of *Pinus* in mixtures with *Eucalyptus*, it is based on the principle that the existing bleaching sequence is the one that is appropriate for *Eucalyptus.*

The pulps constituted by different fractions of eucalyptus and *Pinus taeda* achieved intermediary consumption of active chlorine amongst the 100% fractions, the greater the proportion of *Pinus taeda*, the greater the consumption of total active chlorine. This is a phenomenon that has been demonstrated irrespective of the species used in the study, as this behavior has been observed in both the mixture of eucalyptus hybrids with *Pinus taeda* and in the mixture of *E. globulus* with *Pinus taeda*.

The term bleachability is used to describe the ease of bleaching a certain pulp. There is no standard method for evaluating the bleachability of pulp, and there is not even a standard definition associated with the notion of bleachability, which makes it difficult to explain the different conclusions in different studies. The method normally used is that which uses the consumption of chemical reagents per unit of lignin from the pulp (kappa number), to achieve a certain brightness. In this study we will use this method for the pulps pre-bleached with oxygen.

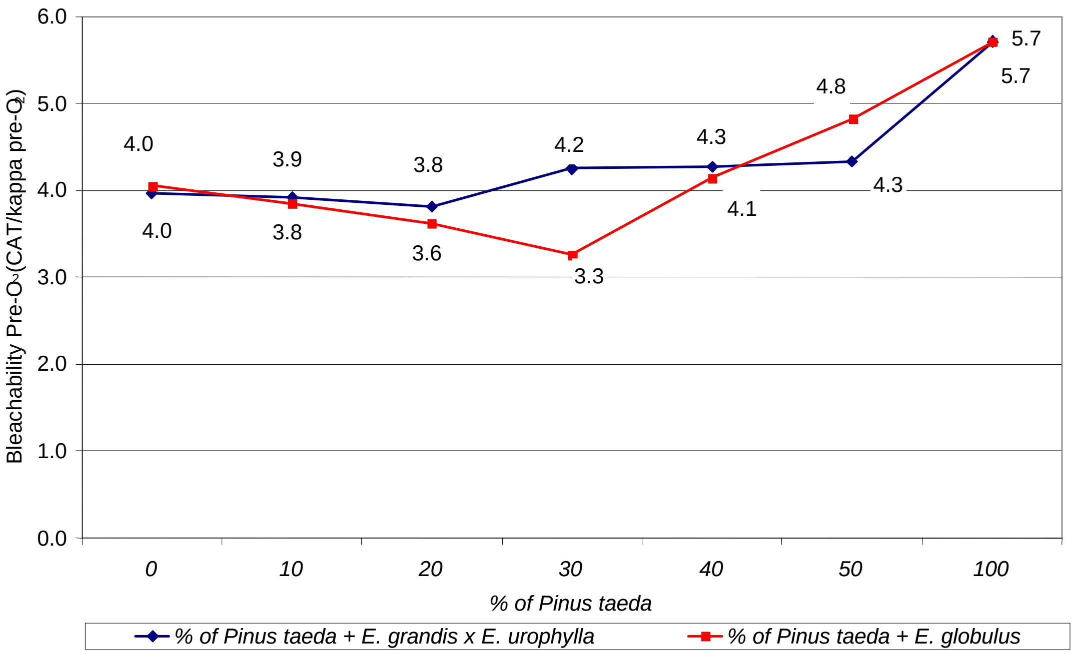


Figure 6 – Bleachability after Pre-O_2.

Pulp from *Pinus taeda* is noted to be more difficult to bleach than that from *Eucalyptus* (5.7 against 4.0 TAC/#k). This could be explained by the greater presence of hexenuronic acids in the eucalyptus pulp, and consequently by its removal in the acid hydrolysis (A) stage, and also because of the greater lignin content in *Pinus taeda* pulp.

The results for the mixture of *Pinus taeda* with eucalyptus hybrid indicate that there are no great alterations in bleachability. That is, up to a fraction of 50% wood from *Pinus taeda* the eucalyptus bleachability characteristics prevail. However, despite the lack of results, it is expected that as the fraction of *Pinus taeda* is increased, the level of hexenuronic acids will be reduced, both by the lower intensity of formation, and by the more severe cooking conditions, which will destroy the hexenuronic acids formed.

The mixture of *Pinus taeda* with *E. globulus* shows values that are difficult to understand. As the fraction of *Pinus taeda* is increased, the bleachability of the pulp after delignification with oxygen improves, reaching the lowest value (3.3 kg TAC /#k) with 30% of *Pinus taeda*. From this point on, the bleachability of the pulp obtained by the mixture of wood referred to begins to fall, until obtaining 4.5 kg TAC /#k with 50% *Pinus taeda*. There are other factors, save for the hexenuronic acids, which interfere in the bleachability of the pulp, such as the quantity and nature of the residual lignin, and also the level of metals. Despite the kappa numbers after the stage with oxygen being similar, those obtained after cooking were different, and it is in this stage of the process that the main factors are created that will interfere in the bleachability of the pulp. This fact could also indicate the need for the optimization of bleaching of pulps from mixtures of *Eucalyptus* and *Pinus*.

Figure 7 presents the results for viscosity of bleached pulps. The solution viscosity of pulp estimates the average degree of cellulose fiber polymerization. So the viscosity empirically measures the level of chemical degradation of fibers. Several studies have used viscosity measurements as a way to predict the strength properties of pulp.

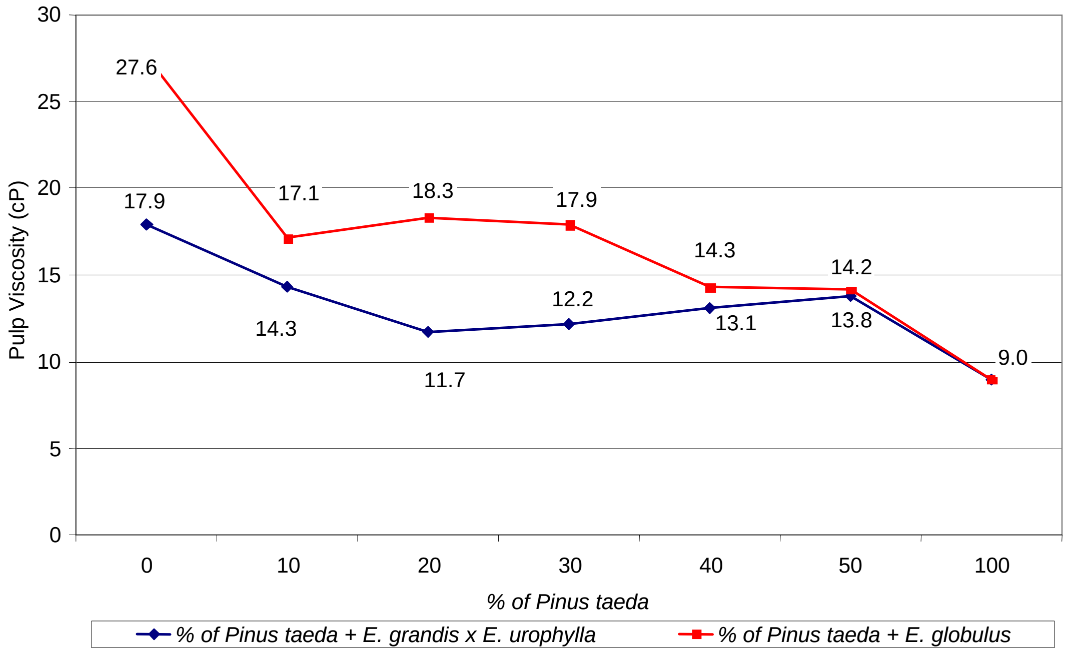


Figure 7 – Pulp viscosity.

The viscosity of the pulps evaluated decreases as greater proportions of *Pinus taeda* are used in the mixtures.

The viscosity of a pulp solution estimates the degree of cellulose fiber polymerization. The viscosity indicates the relative degradation of the fiber during the pulp production process. It must be stressed that the viscosity obtained for pulp from *Pinus taeda* can be considered typical for the species in question, and the comparison of pulp viscosity for hardwoods and softwood trees as a quality parameter can lead to erroneous conclusions.

The objective of the whole bleaching process is to achieve high final brightness. However, this brightness must be stable, which unfortunately does not happen. The brightness of pulp falls during storage and so its reversion is considered to be one of the main specifications for market pulps. Figure 8 presents the results of brightness reversion in the pulps evaluated.

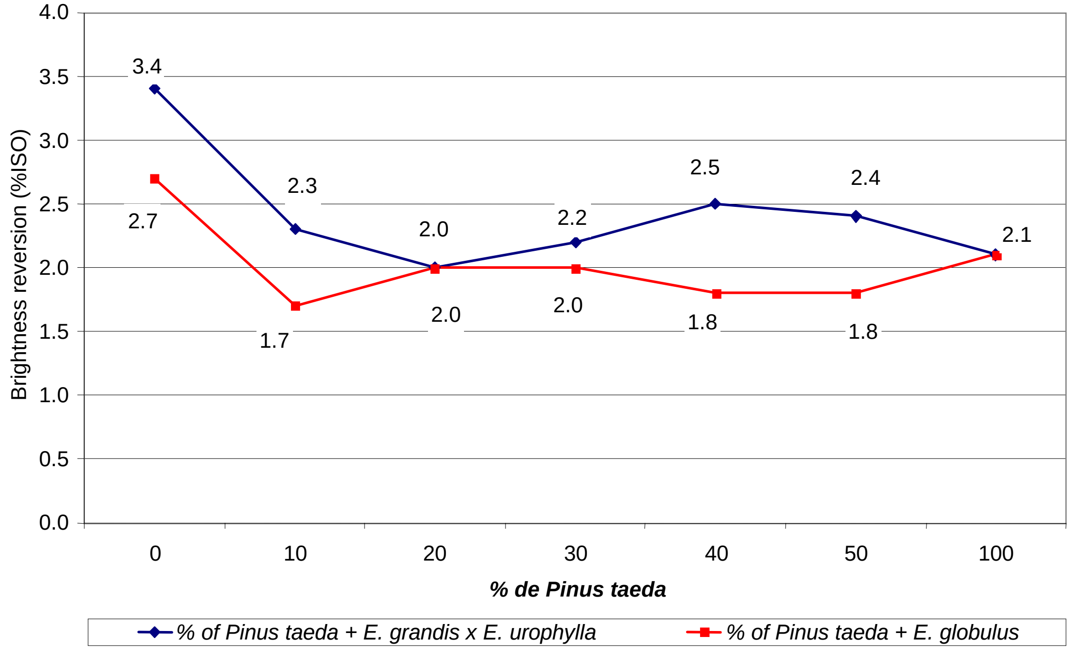


Figure 8 – Brightness reversion in pulps.

According to Colodette et al. (4), under certain conditions, pulps from eucalyptus bleached to high levels of brightness, present low stability. The causes of this problem have not been identified, so it has not been possible to find a solution. The interaction of environmental factors such as light, temperature and humidity, associated with residual lignin, uronic acids and oxidized carbohydrates have been considered the main cause of the reversion of brightness. The authors have also concluded that bleaching sequences than have a final P stage produce pulps with less brightness reversion and lower levels of reducer groups compared with sequences that end with a stage D.

Brightness is one of the most important quality parameters for commercial pulps, and it should be maintained even after transportation and storage. Brightness reversion is, however, a complex phenomenon affected by several factors, such as: hexenuronic acid (HexA) and its degradation products, residual lignin remaining in bleached pulp, oxidized carbohydrate structures formed during pulp production, metals, some extractives, as well as chlorinated structures (11).

The most part of reversion happens in the dark, in the pulp bales. Therefore, reversion reactions induced by light have an effect of little significance, limited to the surface of the bales. Inside the pulp bales the brightness reversion is initiated by condensation reactions, which require active sites such as carbonyl groups. These groups are present in bleached pulp, caused by poor pulp washing, non-selective lignin reactions, impacting the generation of these groups in the pulp chain.

Brightness reversion on pulp from *Pinus* is smaller when compared to pulps from eucalyptus, which could be explained by its lower level of hexenuronic acids. It is also interesting to note than right in the first fraction of the mixture (10% *Pinus*) brightness reversion in bleached pulp falls a lot, not altering significantly until the 100% *Pinus* fraction. These observations are valid for the two mixtures tested, despite the lower levels of brightness reversion observed in the mixtures of *E. globulus* and *Pinus taeda*.

Torres et al. (12) bleached *Pinus tecunumanii* using the following bleaching sequences: ODEoDED, ODEopDED, O/ODEoDED and O/ODEopDED. Total active chlorine consumption varied between 57 and 102 kg ClO_2 and Cl_2 (kg/odt), for brightness of 90% ISO. The viscosity of the pulps for the sequences evaluated was between 11.0 and 15.3 cP, whilst brightness reversion varied between 2.3 to 3.1 %ISO.

Robles et al. (13) evaluated various bleaching sequences in eucalyptus pulps in order to minimize the chlorine dioxide consumption. In comparing the sequences D_{hot}(EOP)DP and D_{hot}(EOP)D(PO), the total active chlorine (TAC) used to obtain pulp with 92% ISO brightness was, respectively, 46.6 and 42,1 kg of total active chlorine. The viscosity of the pulps in the sequences referred to varied between about 11 and 13 cP.

4. Conclusions

Kappa numbers for pulps after pre-delignification with oxygen did not level out, despite the greater efficiency observed for pulp produced from *Pinus taeda*. It is believed the hypothesis tested in the study would have been confirmed if more severe conditions had been used in the pre-delignification with oxygen stage for pulps from *Pinus taeda* and their mixtures.

Optimizations are necessary in order to get better results in terms of chemical consumption in bleaching.

Pulps constituted of different fractions of eucalyptus and *Pinus taeda* obtained intermediary active chlorine consumption amongst 100% fractions, the greater the proportion of *Pinus taeda* being, the greater the consumption of total active chlorine.

In conclusion, manufacturing units that want to produce a differentiated kind of pulp with a high resistance to tearing, to get higher productivity from paper machines, or even to produce special, low-gram papers, must consider the addition of small proportions of *Pinus* to *Eucalyptus*.

5. References

1. FOELKEL, C.E.B. Estrutura da madeira. Belo Oriente: Cenibra. 1977. 84 p.

2. CHEN, R.; GARCEAU, J.J.; KOKTA, B.V. Hardwood mixed with softwood in kraft pulping. Tappi, Atlanta, v. 1, n. 7, p. 35-38, 1978.

3. OLIVEIRA, R.C.; FOELKEL, C.E.B.; GOMIDE, J.L. Misturas de madeiras de *Pinus strobus* var. *chiapensis* e *Eucalyptus urophylla* na polpação Kraft. **O Papel**, São Paulo, v. 42, n. 1, p.67-78, jan. 1981.

4. COLODETTE, J.L.; GOMES, C.M.; RABELO, M.; EIRAS, K.M.M. Progress in Eucalyptus kraft pulp bleaching. In: **2nd COLÓQUIO INTERNACIONAL SOBRE CELULOSE DE EUCALIPTO**, Concepción, 2005. Anais…Concepción, 2005.

5. COLODETTE, J.L., GOMIDE, J.L., SALLES, D.V.C. et al. Factors affecting kraft pulp bleachability with oxygen derived chemicals. In: **INTERNATIONAL NON-CHLORINE BLEACHING CONFERENCE**, 1996, Orlando. Anais. Orlando: TAPPI, 1996. p.1-20.

6. SINGH, R.P. Oxygen bleaching. In: **The bleaching of pulp**. 3 ed. Atlanta: Tappi Press, 1979. cap.7, p.159-209.

7. SALVADOR, E., OLIVEIRA, R.C., COLODETTE, J.L., GOMIDE, J.L. Efeito da deslignificação com oxigênio nas propriedades físico-mecânicas de polpas kraft. In: CONGRESSO INTERNACIONAL DE CELULOSE E PAPEL DA ABTCP, São Paulo, 2000. **Anais**. São Paulo: ABTCP, 2000.

8. PÓVOAS, T.M.; FERREIRA, L.G.; VAN ZELLER, C.A.; CARVALHO, M.G. Optimização de um duplo estágio de oxigênio na deslenhificação de pastas kraft de Eucalyptus globulus. In: **CONGRESSO IBEROAMENRICANO DE INVESTIGACIÓN EM CELULOSA Y PAPEL**, Córdoba, 2004. Anais... Córdoba: CIADICYP, 2004.

9. BASSA, A.G.M.C., SILVA Jr. F.G.S., SACON, V.M. BASSA, A. Advantages and disadvantages of the Lo-Solids® kraft pulp production process based on *Eucalyptus grandis* x *Eucalyptus urophylla* and *Pinus taeda* wood chip mixtures. In: **TAPPI 2007 ENGINEERING, PULPING AND ENVIRONMENTAL CONFERENCE**, 2007. Jacksonville, Florida. **Proceedings**. Jacksonville: TAPPI, 2007.

10. LI, J.; GELLERSTEDT, G. On the structural significance of Kappa number measurement. In: **INTERNATIONAL SYMPOSIUM WOOD PULPING CHEMICAL**, 9; Montreal, 1997. **Proceedings**. Montreal: TAPPI, 1997. P56-71.

11. LIITIÄ, T AND TAMMINEN T. How to evaluate the kraft pulp brightness stability? In: **3rd INTERNATIONAL COLLOQUIUM ON EUCALYPTUS PULP**. Belo Horizonte, 2007. **Anais**. Belo Horizonte, 2007.

12. TORRES, L.F., MELO, R., COLODETTE, J.L. **Revista Árvore** Vol.29 nº.3 Viçosa, Maio/Junho 2005.

13. ROBLES, Y.A.M., SOUZA, L.C., FILHO, C.L. Avaliação de diferentes tecnologias de branqueamento para obtenção de polpa kraft de eucalipto. **O Papel**, Julho de 2006.

Mixed Brazilian Eucalyptus and Pine Species - Bleaching Evaluation

Francides Gomes da Silva
Ana Gabriela Monnerat Carvalho Bassa
Flavia Schmidt
Marcelo Rodrigues da Silva
Alexandre Bassa
Vera Maria Sacon

Introduction

- Main raw material sources for pulp and paper production in Brazil - Pine and *Eucalyptus*
- Advantages in Brazil - development of eucalyptus-based short-fiber pulp and its success on the international market
- *Eucalyptus grandis* x *Eucalyptus urophylla* hybrids / pine

Introduction

- Marked differences when comparing these two genera - amongst them the length of the fibers.
- The fibers from the genus *Eucalyptus* present a length of between 0.5 and 1.5mm
- Pine presents long fibers (measuring between 3 and 6mm in length)

  - papers with high physical-mechanical resistance
  - allows higher paper machine speed due to the greater resistance of wet and dry sheets, and easier drainage
  - greater efficiency in paper production, and lower production costs

Objectives

- This study analyzes the results of kraft pulp bleaching by the (OO)(AD)EopDP bleaching sequence, using pulps produced with mixtures of:

  - *Eucalyptus grandis* x *Eucalyptus urophylla* hybrid and *Pinus taeda* wood chips

  - *Eucalyptus globulus* and *Pinus taeda* wood chips

Materials and Methods

- Wood species used in this study were:

  - Hybrid of *Eucalyptus grandis x Eucalyptus urophylla* at 7 years old, from the Votorantim Celulose e Papel (VCP) commercial forest

  - *Eucalyptus globulus* of 7 years old from a trial set at Aracruz Guaíba

  - *Pinus taeda* of *9* years old from the Klabin commercial forest

Materials and Methods

Eucalyptus grandis x Eucalyptus urophylla	***Pinus taeda***	***E. globulus***	***Pinus taeda***
100%	0%	100%	0%
90%	10%	90%	10%
80%	20%	80%	20%
70%	30%	70%	30%
60%	40%	60%	40%
50%	50%	50%	50%
0%	100%	0%	100%

Materials and Methods

- The pulps were produced by Lo-solids® cooking simulations

Eucalyptus grandis x Eucalyptus urophylla + Pinus taeda	Kappa Number	Lignin content (%)	HexA. mmol/kg	Viscosity. cP	Brightness. %ISO
0% Pinus	17.9	3.47	50.41	93.2	49.2
10% Pinus	19.1	2.56	56.06	46.0	50.7
20% Pinus	19.0	3.02	51.25	36.0	47.6
30% Pinus	20.3	2.70	39.57	35.1	43.9
40% Pinus	21.0	3.78	40.97	30.1	43.6
50% Pinus	22.1	3.93	43.49	32.5	36.9
100% Pinus	25.6	3.59	30.35	26.4	33.5
E. globulus*.+ *Pinus taeda	**Kappa Number**	**Lignin content (%)**	**HexA. mmol/kg**	**Viscosity. cP**	**Brightness. %ISO**
0% Pinus	17.2	2.73	50.50	82.8	52.9
10% Pinus	17.9	3.88	56.59	43.3	51.8
20% Pinus	19.3	3.56	55.68	35.4	50.1
30% Pinus	20.7	3.28	50.03	34.5	45.4
40% Pinus	21.2	3.75	47.76	35.0	44.3
50% Pinus	22.1	3.54	42.62	33.7	42.3
100% Pinus	25.6	3.59	30.35	26.4	33.5

Materials and Methods

Conditions	Bleaching Stages					
	O/O	**A/**	**D**	**(EPO)**	**D**	**P**
Consistency, %	12	12	12	10	10	10
Time, min	15/45	120	13	65	120	120
Temperature, ^{0}C	95/105	90	85	85	75	80
Pressure, KPa	600/450	-	-	4,13	-	-
Final pH	11.0	3.0	2.5	11.0	4.5	11.0
Caustic, kg/odt	20/0	-	-	-	-	-
Oxygen, kg/odt	15/7	-	-	80	-	-
Kappa Factor	-	-	0.18/0.20	-	-	-
Chlorine Dioxide as Cl_2, kg/odt	-	-	17.8-26.8	-	8.0	-
Hydrogen Peroxide, kg/odt	-	-	-	4.0-8.0	-	3.0-12.0

Materials and Methods

Parameters	Norms
Kappa Number	TAPPI – T236 cm-85
Viscosity	TAPPI – T230 om-94
Brightness	ISO 2469-1980; ISO 2470-1977; ISO 3688-1980.
Brightness reversion	TAPPI-UM 200
Hexenuronic acids	Chai et al. (2001)

Results and Discussion

Oxygen Delignification

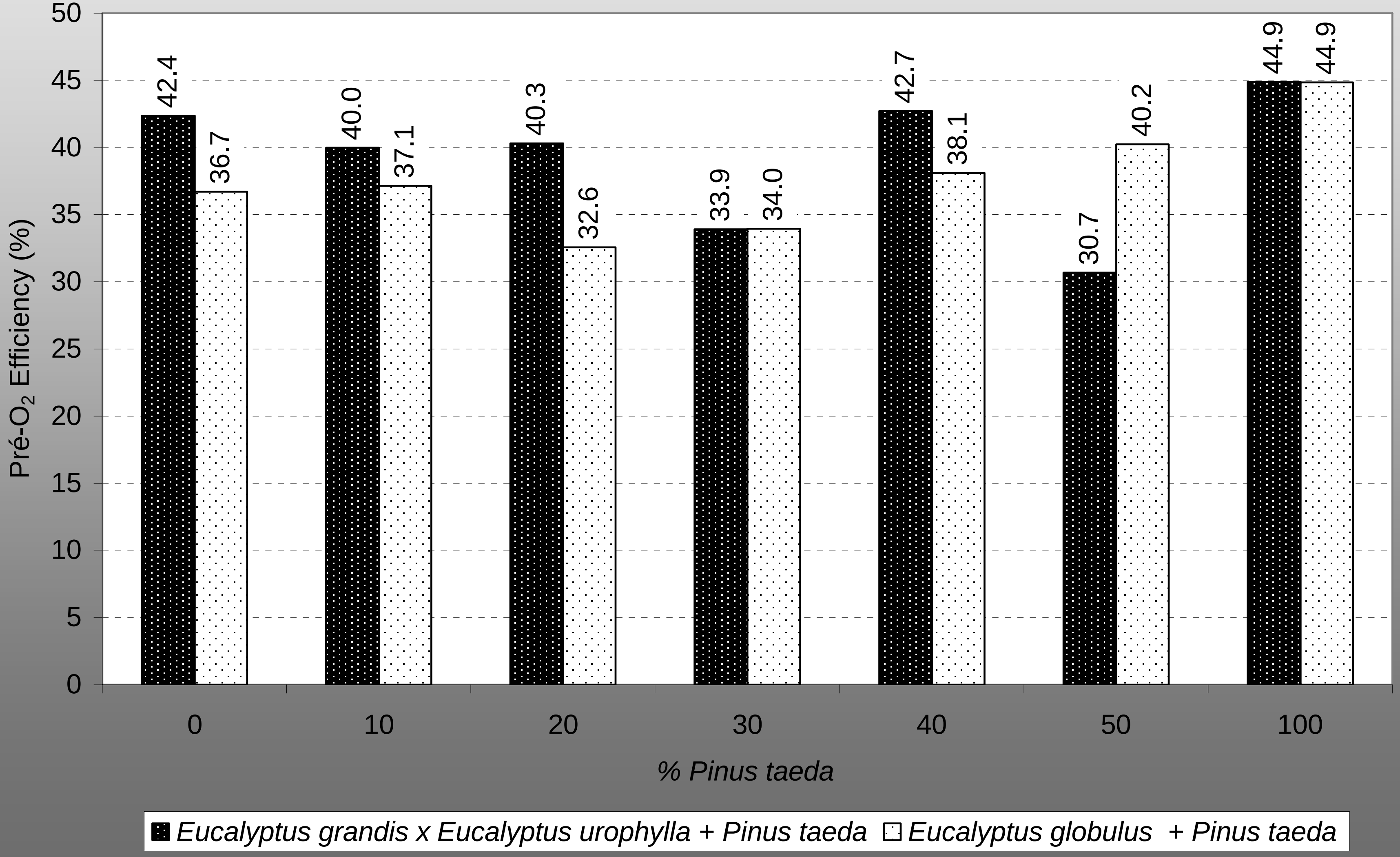
- Hypothesis tested in this study is that after this stage kappa numbers would level out

  - owing to the difference in efficiency in the pre-delignification stage with oxygen between pulp produced from long and short fibers

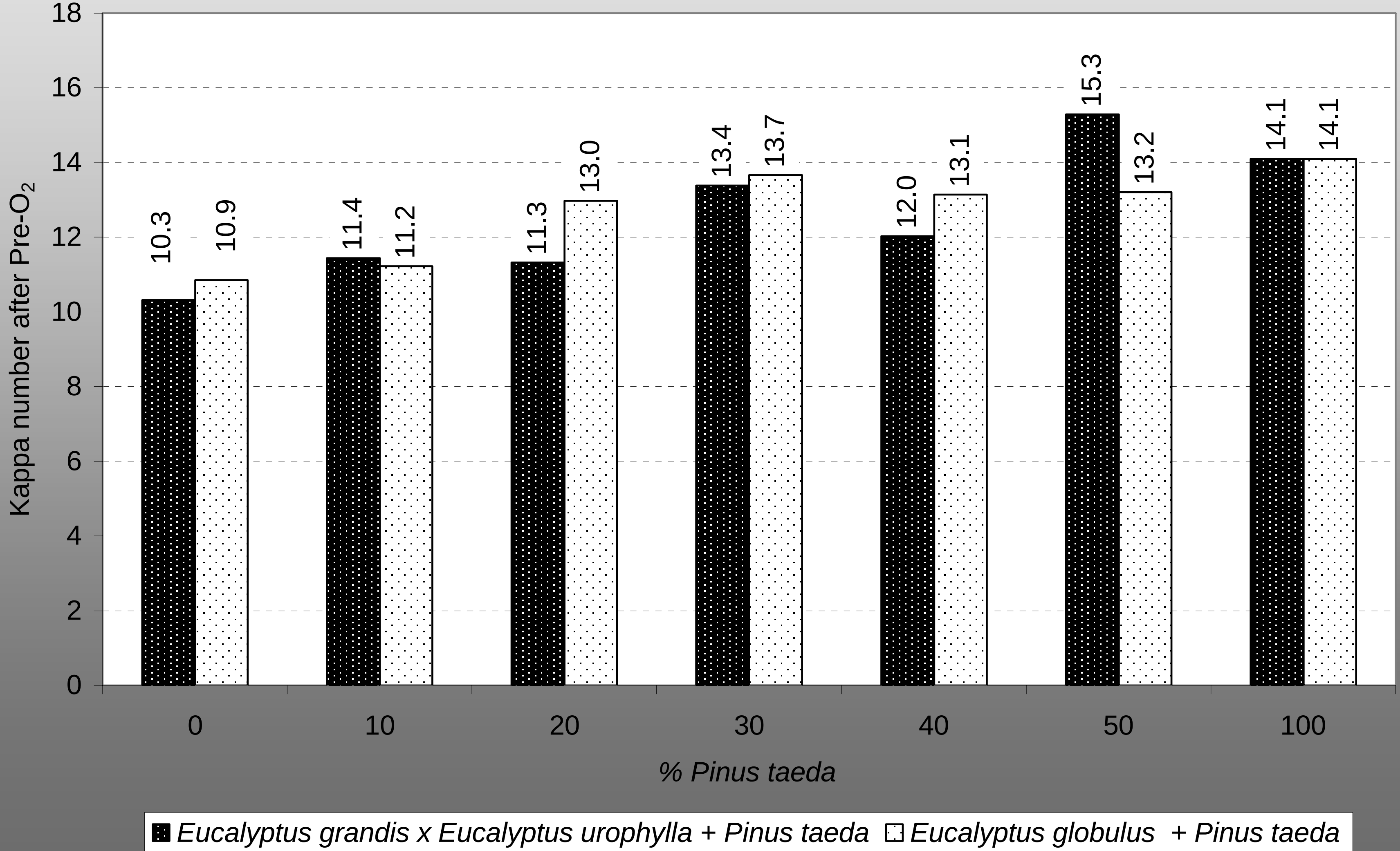
  - *Pinus taeda* pulp presents a higher level of lignin, lower level of hexenuronic acids and a higher kappa number at the entry of pre-delignification with oxygen

  - Eucalyptus pulps have lower levels of lignin, higher levels of hexenuronic acids and lower kappa numbers after pulping kappa numbers

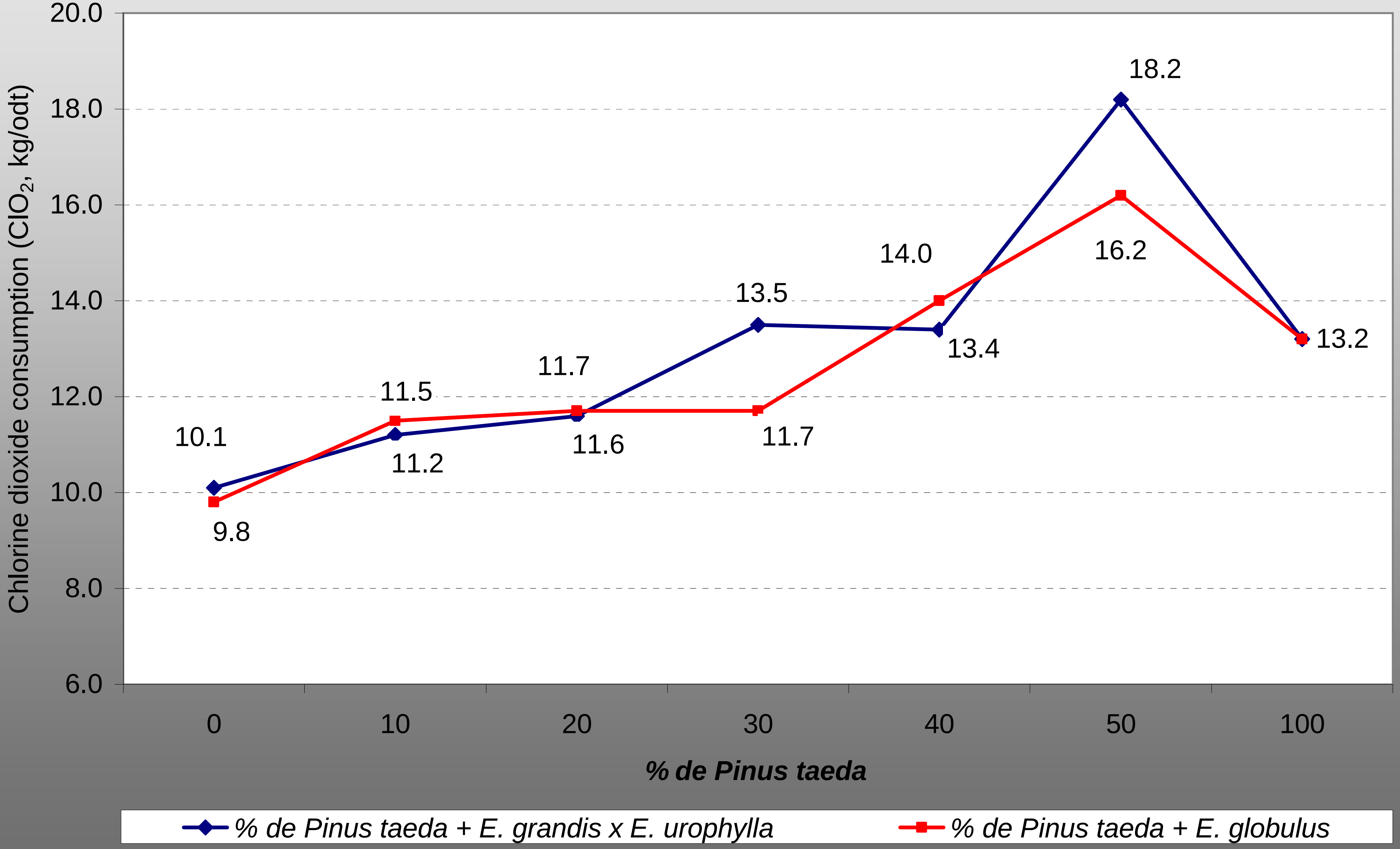
Oxygen Delignification



Oxygen Delignification

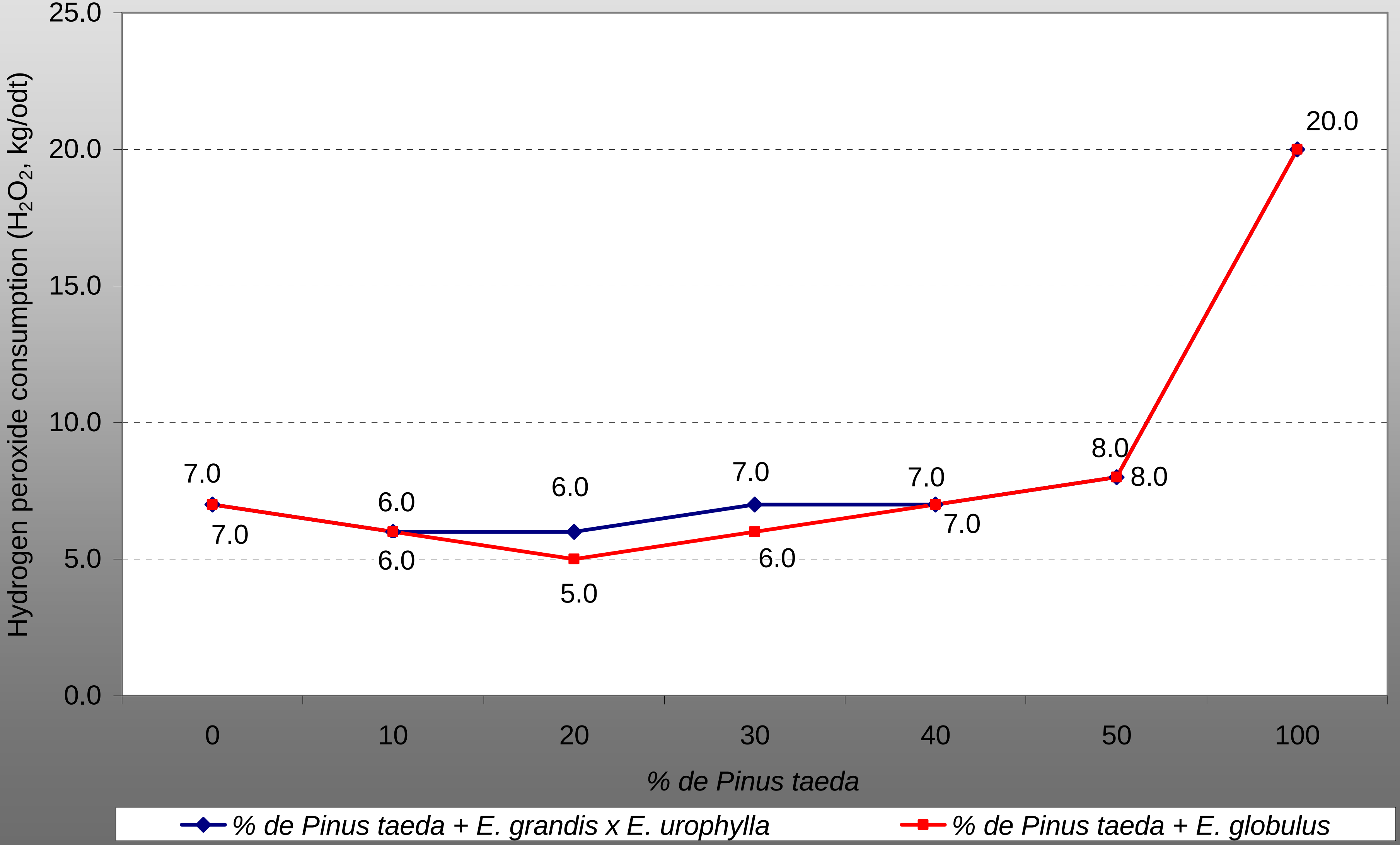


Bleaching



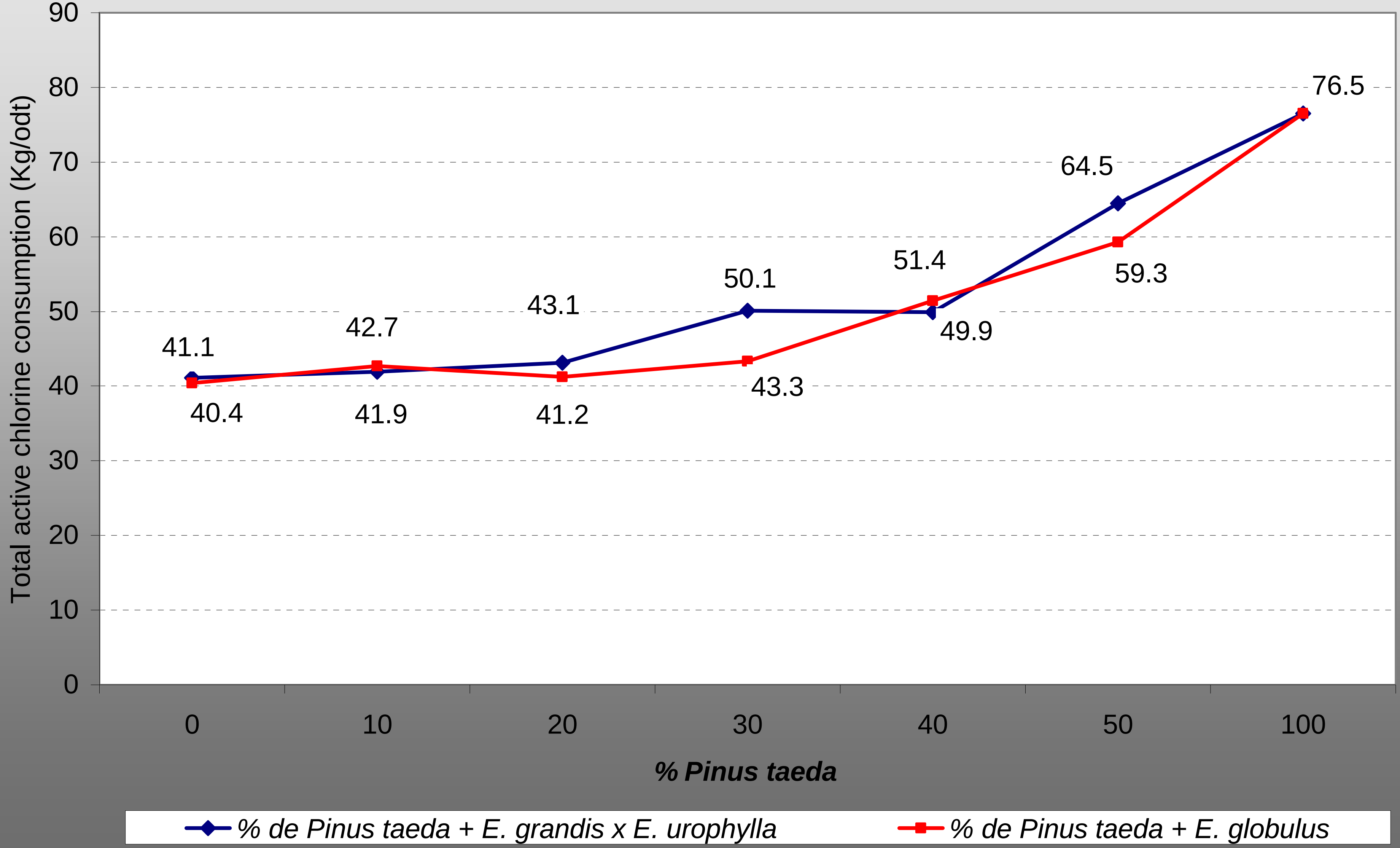
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
Chlorine dioxide consumption (ClO2, kg/odt)
18.2
14.0
16.2
13.5
13.4
13.2
11.7
11.5
10.1
11.7
11.6
11.2
9.8
0
10
20
30
40
50
100
% de Pinus taeda
% de Pinus taeda + E. grandis x E. urophylla
% de Pinus taeda + E. globulus

Bleaching



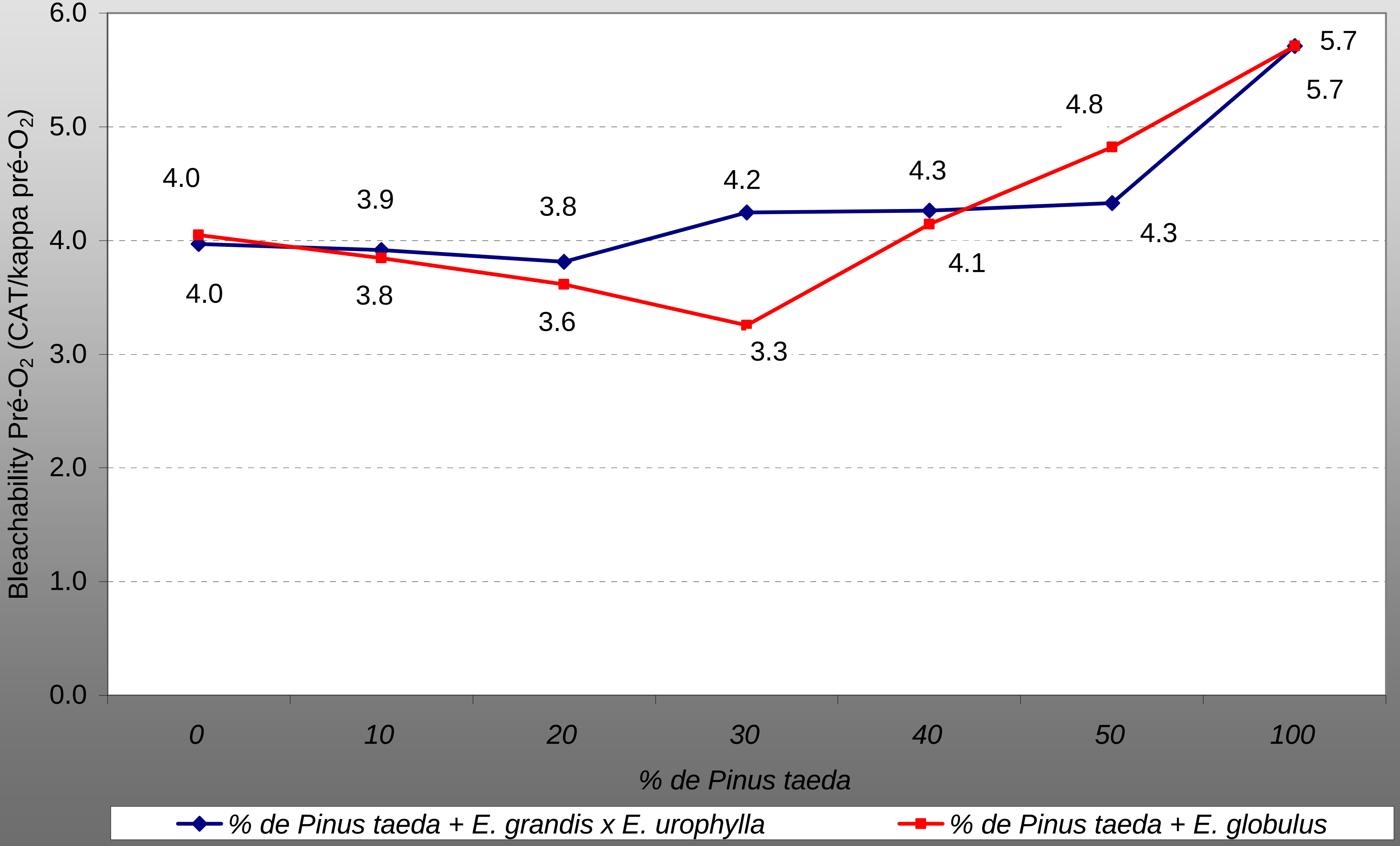
25.0
20.0
15.0
10.0
5.0
0.0
Hydrogen peroxide consumption (H_2O_2, kg/odt)
7.0
7.0
6.0
6.0
6.0
5.0
7.0
6.0
7.0
7.0
8.0
8.0
20.0
0
10
20
30
40
50
100
% de Pinus taeda
% de Pinus taeda + E. grandis x E. urophylla
% de Pinus taeda + E. globulus

Bleaching



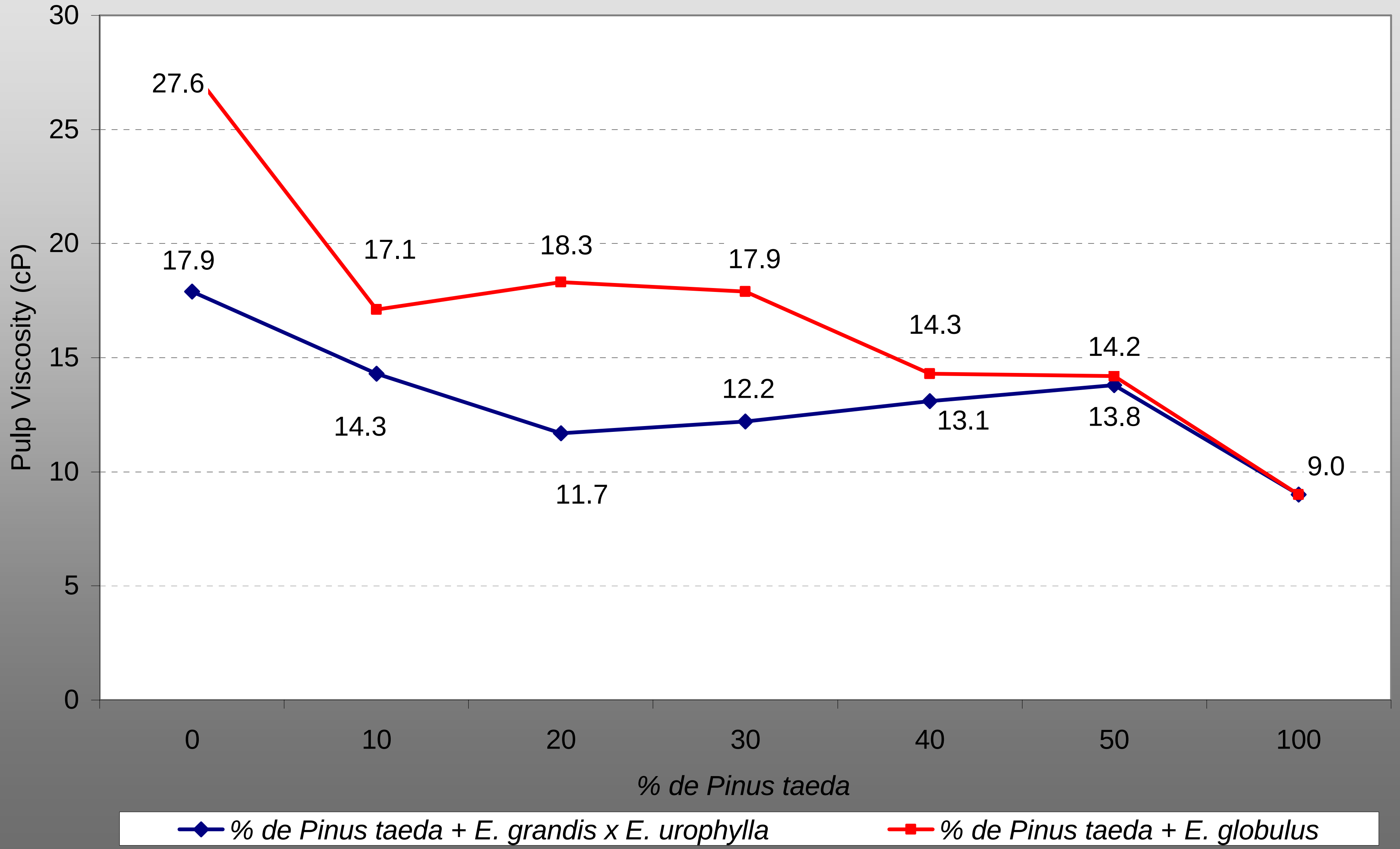
90
80
70
60
50
40
30
20
10
0
Total active chlorine consumption (Kg/odt)
76.5
64.5
51.4
59.3
50.1
43.1
42.7
41.1
49.9
43.3
40.4
41.9
41.2
0
10
20
30
40
50
100
% Pinus taeda
% de Pinus taeda + E. grandis x E. urophylla
% de Pinus taeda + E. globulus

Bleaching



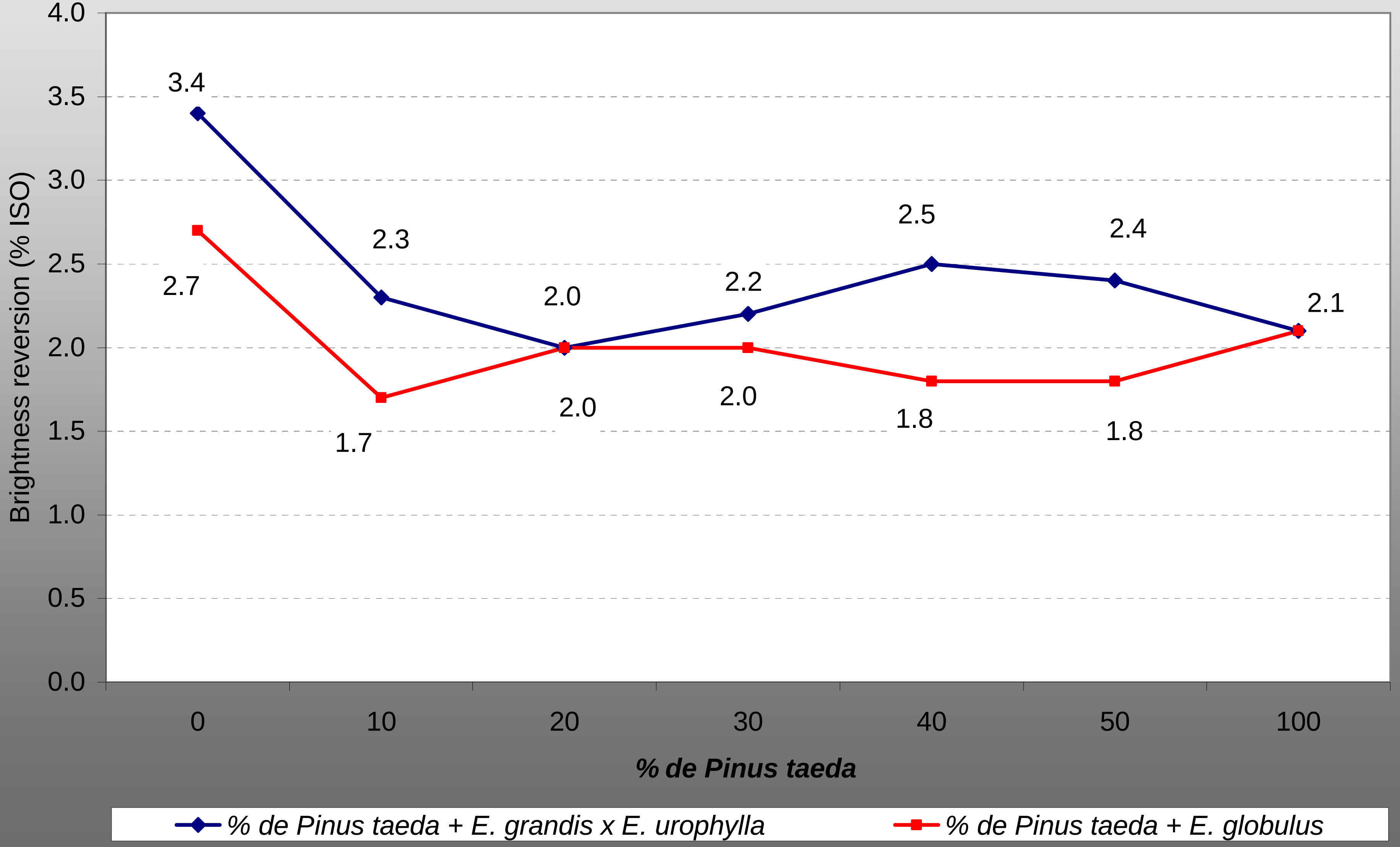
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Bleachability Pré-O2 (CAT/kappa pré-O2)
4.0
3.9
3.8
4.2
4.3
4.3
5.7
4.0
3.8
3.6
3.3
4.1
4.8
5.7
0
10
20
30
40
50
100
% de Pinus taeda
% de Pinus taeda + E. grandis x E. urophylla
% de Pinus taeda + E. globulus

Bleaching



30
25
20
15
10
5
0
Pulp Viscosity (cP)
27.6
17.9
17.1
18.3
17.9
14.3
14.2
14.3
11.7
12.2
13.1
13.8
9.0
0
10
20
30
40
50
100
% de Pinus taeda
% de Pinus taeda + E. grandis x E. urophylla
% de Pinus taeda + E. globulus

Bleaching



Brightness reversion (% ISO)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.4
2.3
2.0
2.2
2.5
2.4
2.1
2.7
1.7
2.0
2.0
1.8
1.8
0
10
20
30
40
50
100
% de Pinus taeda
% de Pinus taeda + E. grandis x E. urophylla
% de Pinus taeda + E. globulus

Conclusions

- Kappa numbers for pulps after pre-delignification with oxygen did not level out despite the greater efficiency observed for pulp produced from *Pinus taeda*
  - hypothesis tested in the study would have been confirmed if more severe conditions had been used in the pre-delignification with oxygen stage for pulps from *Pinus taeda* and their mixtures
- Optimizations are necessary in order to get better results in terms of chemical consumption in bleaching

Conclusions

- Pulps constituted of different fractions of eucalyptus and *Pinus taeda* obtained intermediary active chlorine consumption amongst 100% fractions, the greater the proportion of *Pinus taeda* being, the greater the consumption of total active chlorine

- In conclusion, manufacturing units that want to produce a differentiated kind of pulp with a high resistance to tearing, to get higher productivity from paper machines, or even to produce special, low-gram papers, must consider the addition of small proportions of *Pinus* to *Eucalyptus*.

Thank you for your attention!

Questions?