CONVERSION OF THE KRAFT PROCESS IN SODA-DDA (DISODIUM SALT OF 1,4-DIHYDRO-9,10-DIHYDROXY ANTHRACENE) FOR EUCALYPTUS

F. G. Silva Júnior
Research Engineer
Votorantim Pulp & Paper
Luiz Antônio,SP 14210-000
Brazil

L. E. G. Barrichelo
Titular Professor
University of São Paulo
Piracicaba, SP 13418-900
Brazil

ABSTRACT

In this research the possibility of converting the kraft pulping process of *Eucalyptus grandis* in soda process by the addition of disodium salt of 1,4-dihydro-9,10-dihydroxi anthracene (DDA) was investigated Besides the reduction/elimination of sulfidity, the objective was to attain the reduction of the alkaline charge and energy consumption without affecting the process parameters and pulp quality.

0.04%(w/w) of DDA was the charge that showed the best results for the process variables and also for the pulp; it was thus possible to reduce the active alkali from 14 to 13% (approximately 7%).

After having fixed the levels of DDA and active alkali, a reduction in hte H factor of nearly 20% was reached without affecting the pulp quality and process characteristics.

The effect of sulfidity was also evaluated on *Eucalyptus grandis* cookings with 0.04% of DDA, active alkali of 13% and H factor of 522. The sulfidity had a beneficial effect, specially for the pulp viscosity; however, the ideal sulfidity level was between 5 and 10%.

DDA shows good effects in soda and kraft pulping process of *Eucalyptus grandis* chips allowing the reduction of chemical charge (especially sulfidity) and energy consumption during cooking without damaging the pulp quality or process characteristics.

Brazil is the one of biggest eucalyptus pulp producers in the world. The development of pulping process technologies lead to the production of eucalyptus pulp with international quality patterns and reaching markets closed to short fiber pulps of eucalyptus.

In relation to eucalyptus pulp, the Brazilian position in the world scene should is being reinforced since new mills are being built and some of the existing ones are expanding their production capacities.

Production and enviromental protection are the main challange of pulp industries and the use of chemical additives that increase the efficiency of pulping reactions is a line of research that can be useful to achieve this goal.

The additives that have been showing the best performances are the quinonic compounds. In most of the researchs with quinonic compounds as pulping additives the conclusion is that in general, this kind of compounds are very effective in alkaline pulping process (1-5). Anthraquinone is the most common quinonic compound and is in industrial use in some countries such as United States, Japan, Finland, Brazil and others. The main inconvenience of anthraquinone is its low solubility in the cooking liquor, making it necessary to develop industrial systems that allow the uniform distribuition of this additive in digesters, which is very important for the efficiency of anthraquinone.

Another quinonic coumpound that presents a great potencial as a pulping additive is the disodium salt of 1,4-dihydro-9,10-dihydroxi anthracene (DDA), that is liquid and soluble in the cooking liquor, making its distribution in digesters easier. Despite the large use of DDA in Japan, for hardwood pulping a few studies have been done with this compound (6,7).

The mechanism of DDA is quite similar to that of anthraquinone. DDA has a redox potential of -0.13V, compared to 0.15V for anthraquinone. Therefore, the redox cycle for DDA starts with the reduction of lignin, whereas the cycle for anthraquinone starts with the oxidation of carbohydrates (6-8).

The main objective of this research was to convert the kraft pulping process of *Eucalyptus grandis* in soda-DDA process. Besides the reduction/elimination of sulfidity, the reduction of alkaline charge and energy consumption without loss in the pulp quality was aimed at.

MATERIALS AND METHODS

Chips from 7-years-old *Eucalyptus grandis* trees were used in this research

The research was conducted in 4 stages:
1. DDA charge
2. alkaline charge
3. H factor
4. sulfidity

The cookings were conducted in a stainless steel 20 L rotative digester. On the table below the cooking conditions evaluated in this research are summarized .

I. Summary of cooking conditions

Condition	DDA charge (%)	Active alkali (% as Na_2O)	H fator	Sulfidity (%)
1	-----	14	677	------
2	-----	14	677	------
3	0.04	14	677	------
4	0.06	14	677	------
5	0.08	14	677	------
6	0.10	14	677	------
7	0.04	12	677	------
8	0.04	13	677	------
9	0.04	14	677	------
10	0.04	15	677	------
11	0.04	13	215	------
12	0.04	13	369	------
13	0.04	13	522	------
14	0.04	13	522	5
15	0.04	13	522	10
16	0.04	13	522	15
17	0.04	13	522	20
18	0.04	13	522	25

The following parameters were the same for all conditions:
temperature: 170°C
time to temperature: 60 min.
liquor/wood ratio: 4/1 (L/kg)

For each condition 2 cookings were made and the results are presented as an average of them.

Analytical Methods

After each cooking the pulp was washed and the following parameters were determined:

- total pulp yield: relation between pulp weight (o.d.) and wood weight (o.d.)
- screened pulp yield: relation between screened pulp weight (o.d.) and wood weight (o.d.)
- kappa number - TAPPI T 236 cm-85
- viscosity - TAPPI T 254 cm-85

From each cooking a pulp sample was prepared for refining in a PFI mill according to TAPPI T 248 cm-85. The preparation of handsheets and the determination of strength properties were carried out according to TAPPI T 220 om-83.

RESULTS

The cooking conditions 1 and 2 represent traditional kraft and soda cookings and were used as references in this research.

II. Kraft and soda pulp characteristics

	kraft	soda
total pulp yield (%)	56.1	58.5
screend pulp yield (%)	56.1	58.4
kappa number	19.3	48.7
viscosity (cP)	52.3	30.3

The results on table II show the superiority of the kraft process over the soda. The kraft process was characterized, as expected, by a good screened pulp yield, relatively low kappa number and high viscosity.

The figures 1 to 4 show the results of the strength properties

Fig. 1. Tensile index for soda and kraft pulps

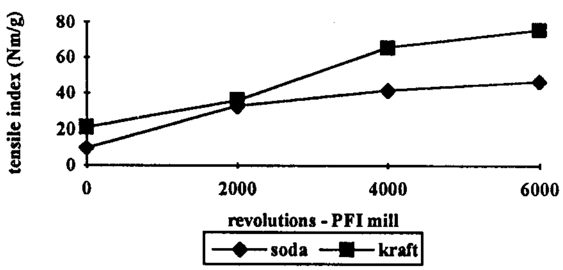


Fig. 2. Burst index for soda and kraft pulps

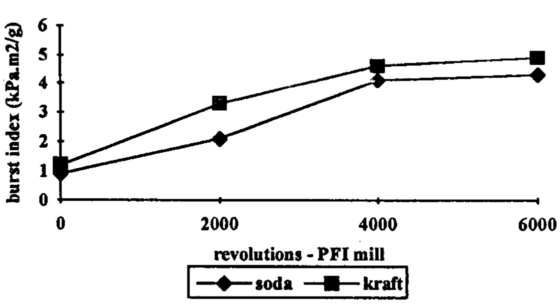


Fig. 3. Tear index for soda and kraft pulps

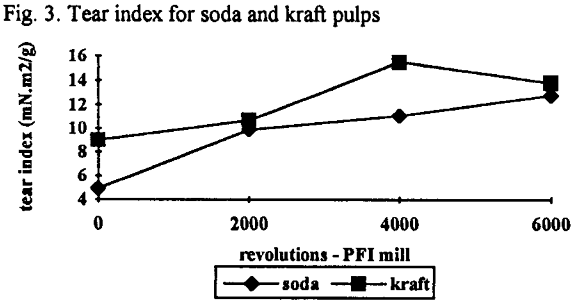
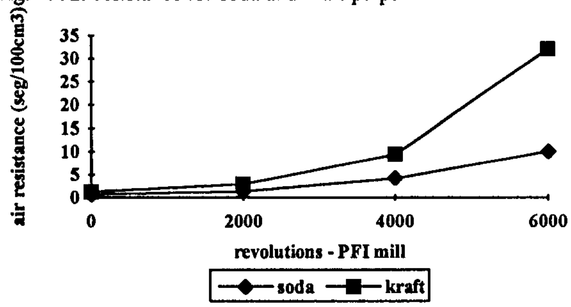


Fig. 4. Air resistance for soda and kraft pulps



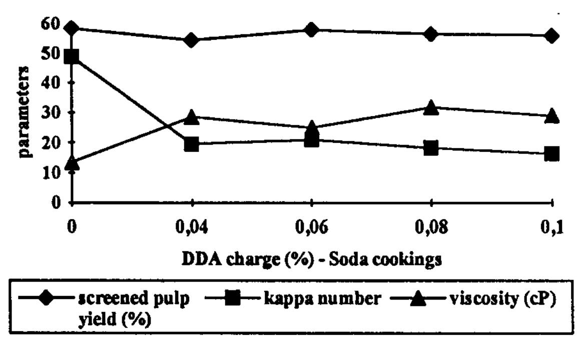
Also in the strength properties the kraft pulps is much superior to soda pulp.

DDA Charge

To determine the best level of the DDA charge, the kappa number and viscosity were considered.

In figure 5 the results of screened pulp yield, kappa number and viscosity are shown.

Fig. 5. Screened pulp yield, kappa number and viscosity for soda-DDA cookings

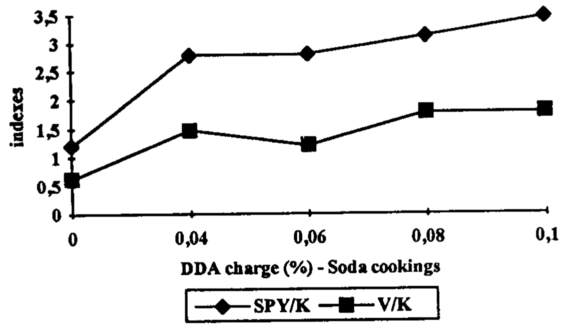


From this figure we can see that DDA has a pronouced effect at charge of 0.04%; the reduction in kappa number is very sharp and there is a significant increase in viscosity. These facts agree with the mechanism proposed for quinonic compounds, increase of delignification rate and carbohydrate protection.

The analysis of the kappa number of the pulps obtained by soda-DDA process show that 0.04% of DDA conducted to a reduction of aproximately 50%, making the process similar to kraft in this topic; however, the adittion of larger charges of DDA lead to a decrease in kappa number but in a shorter scale. The efficiency of DDA, despite its chemical reaction mechanism, is also related to its solubility in the cooking liquor and its greater capacity to penetrate into the chips, being more readly in the reaction site.

Screened pulp yield, kappa number and viscosity are parameters that are strongly related.; the analysis of these parameters should not be done isolatedly and is important to evaluate indexes such as screened pulp yield (SPY)/kappa number (K) and viscosity(V)/kappa number (K). In this research such indexes were used as comparative tools.

Fig. 6. Screened pulp yield (SPY)/kappa number(K) and viscosity (V)/kappa number (K) indexes for soda-DDA cookings



The kappa number reduction lead to an increase in the screened pulp yield(SPY)/kappa number (K) index in the same scale, since the effect of DDA on the screened pulp yield was relatively small.

The addition of DDA to soda cookings led to an increase in viscosity but inferior to kraft pulps. The protection effect of DDA over the carbohydrates is inferior to the sodium sulfide. The association of these two compounds, DDA and sodium sulfide, can lead to great gains in pulp quality and enviromental protection, in relation to a typical kraft process.

The figures 7 to 10 show that the use of DDA in a soda cooking improve the pulp strength properties, leading to results very similar to traditional kraft pulps.

Fig. 7. Tensile index for soda-DDA pulps

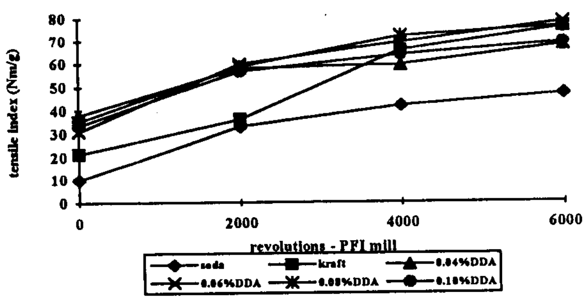


Fig. 8. Burst index for soda-DDA pulps

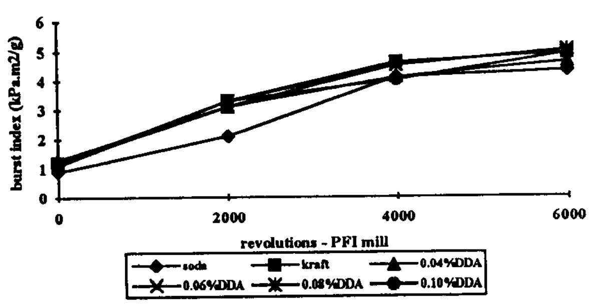


Fig. 9. Tear index for soda-DDA pulps

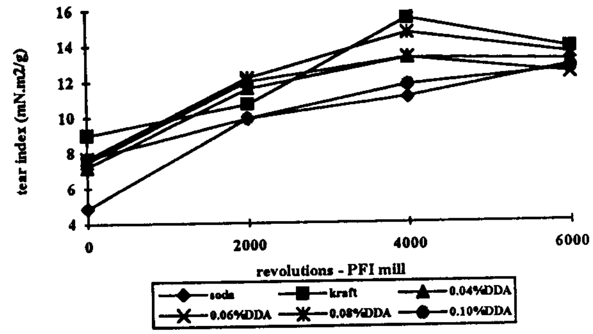
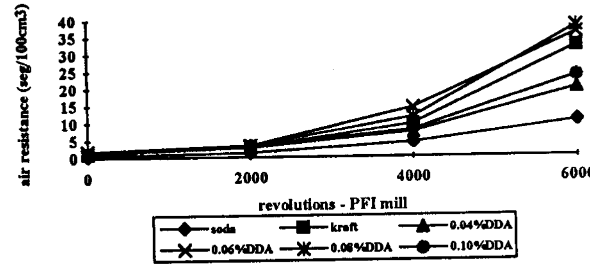


Fig. 10. Air resistance for soda-DDA pulps



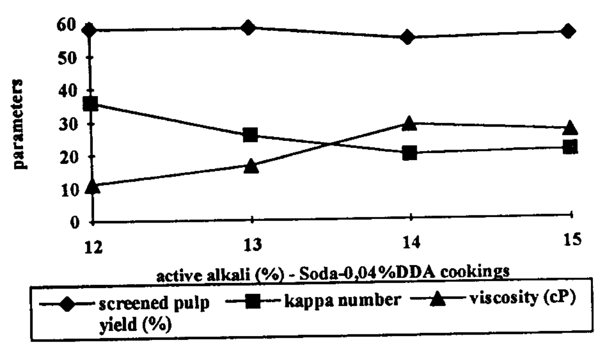
The results of this stage of the research and the economical aspects involved in the use of DDA lead to the conclusion that among the charges tested, 0.04% of DDA was the best.

Alkaline Charge

After having fixed the best level of DDA (0.04%) the objective of the following stage of the research was to evaluate the effect of active alkali in a soda-0.04% DDA cooking of *E. grandis* chips.

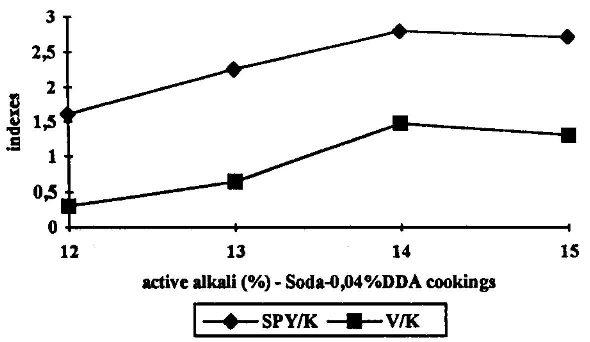
In the figure 11 the results of the effect of active alkali on screened pulp yield, kappa number and viscosity are shown; the screened pulp yield (SPY)/kappa number (K) and viscosity (V)/kappa number (K) indexes are on figures 12.

Fig. 11. Effect of active alkali on screened pulp yield, kappa number and viscosity for soda-0.04%DDA cookings



The active alkali has a pronouced effect on the pulp quality, specially for residual lignin, expressed as kappa number. As shown in this chart, the increase in the active alkali reduces the kappa number and the screened pulp yield.

Fig. 12. Effect of active alkali on screened pulp yield (SPY)/kappa number (K) and viscosity (V)/ kappa number (K) for soda-0.04%DDA cookings



As a consequence of the kappa number reduction, there is an increase in the values of the screened pulp yield(SPY)/kappa number (K) index as the active alkali decreases.

Figures 13 to 16 show the strength properties of soda-DDA pulps with different levels of active alkali.

Fig. 13. Effect of active alkali on tensile index of soda-0.04%DDA pulps

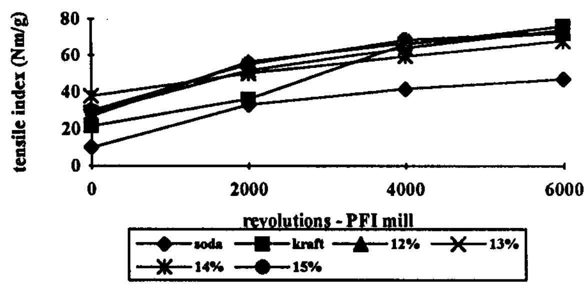


Fig. 14. Effect of active alkali on burst index of soda-0.04%DDA pulps

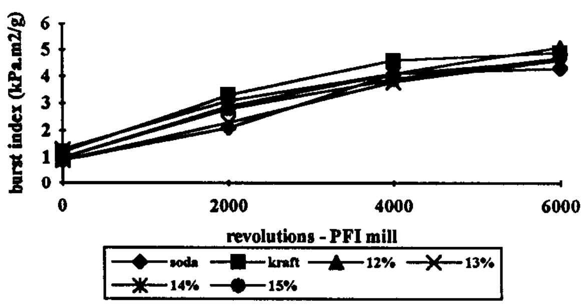


Fig. 15. Effect of active alkali on tear index of soda-0.04%DDA pulps

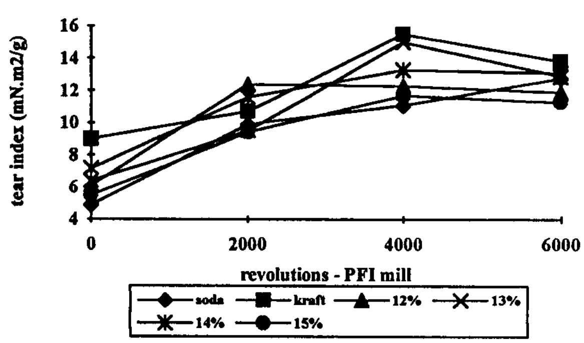
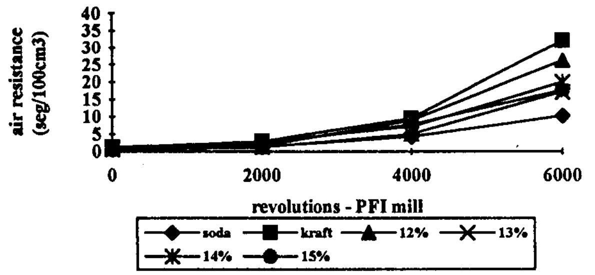


Fig. 16. Effect of active alkali on air resistance for soda-0.04%DDA pulps



The previous figures show that active alkali have a short effect on the pulp characteristics, but the superiority of soda-DDA pulps on traditional soda cooking is noted.

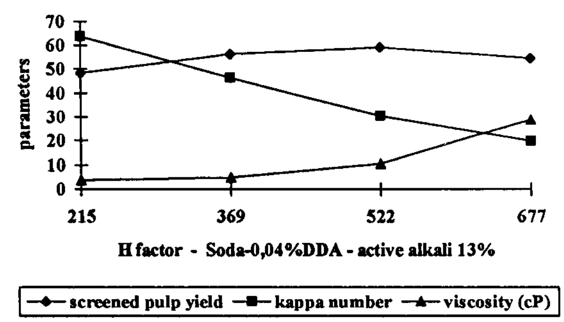
The results of this stage show that the best level of active alkali for soda-0.04%DDA cooking is between 13 and 14%. With the objetive of optimizing the pulping process and obtaining an economy in chemicals, was decided to continue this research with 13% of active alkali.

H Factor

The H factor is an index that can be useful to evaluate the energy consumption in a pulping process. It is related to time and delignification rate that, by its time, is related with temperature.

On the figure below the effect of H factor on screened pulp yield, kappa number and viscosity is shown.

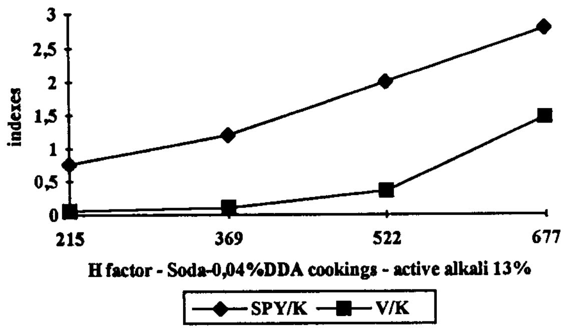
Fig. 17. Effect of H factor on screened pulp yield, kappa number and viscosity for soda-0.04%DDA cookings (active alkali - 13%)



In this figure it can be observed that the increase in H factor leads to an increase in screened pulp yield and a reduction in kappa number. These facts are results of the increase of the delignification reactions which have as a consequence the reduction of rejects and a greater removal of lignin.

We can also observe in figure 17 an increase in viscosity. At this point some considerations should be made: the pulp obtained with low H factor (215) show characteristics of semichemical pulps as high yield and kappa number. For these reasons such analysis of viscosity do not make sense.

Fig. 18. Effect of H factor on screened pulp yield (SPY)/kappa number (K) and viscosity (V)/kappa number (K) indexes for soda-0.04%DDA cookings (active alkali - 13%)



The increase in H factor conduct to an increase in the screened pulp yield (SPY)/kappa number (K) index.

At this stage the influence of H factor on the pulp strength properties was also evaluated.

Fig. 19. Effect of H factor on tensile index of soda-0.04%DDA pulps (active alkali - 13%)

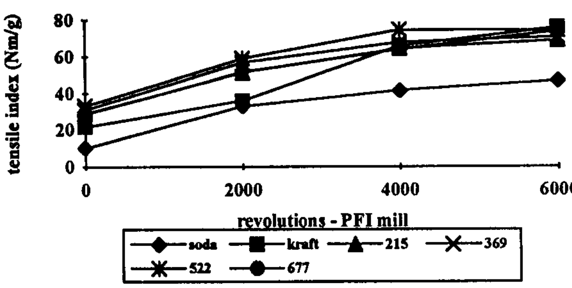


Fig. 20. Effect of H factor on burst index of soda-0.04%DDA pulps (active alkali - 13%)

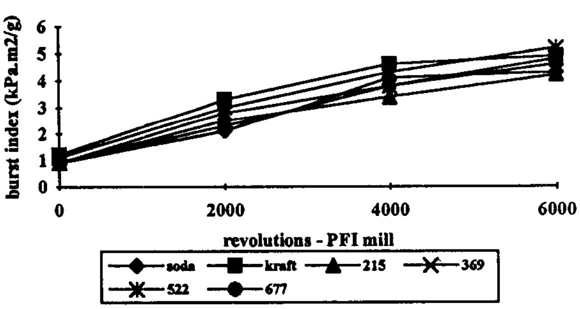


Fig. 21. Effect of H factor on tear index of soda-0.04%DDA pulps (active alkali - 13%)

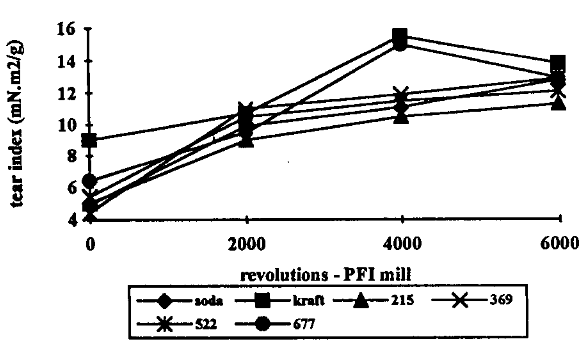
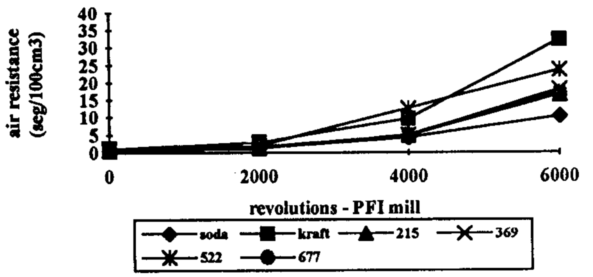


Fig. 22. Effect of H factor on air resistance for soda-0.04%DDA pulps (active alkali - 13%)



The variation of the H factor had low effect on the pulp tensile and burst indexes. The tear index was the pulp property that was directly influenced by the H factor.

Considering the aspects related to pulp quality, specially strength properties, the reduction of H factor to a level around 500 in soda-DDA cookings with active alkali of 13% of *E. grandis* chips, have low effect on the pulp quality.

At the transition from one stage to another the possibility of chemical and energy economy has been considered. In this aspect and considering the results obtained, the best H factor for soda-0.04%DDA pulping with 13% of active alkali of *E. grandis* is 522.

Sulfidity

At the last stage of the research the effect of sulfidity on the soda-0.04%DDA process (active alkali = 13% and H factor = 522) for *E. grandis* chips was evaluated.

The total elimination of sulfur compounds is very difficult according to LIMA (10) since the oil that feeds the lime kiln has sulfur compounds in its composition.

It should also be taken into consideration that in traditional kraft mills, the reduction of sulfidity can make the lime kiln a bottleneck in the production process. This situation can be explained by the fact that with the reduction of sodium sulfide, the sodium hydroxide part is increased in the cooking liquor. The sodium hydroxide is recovered in the stage of the recovery cycle called recausticizing that involves the addition of calcium hydroxide to the green liquor to convert sodium carbonate into sodium hydroxide. Therefore, an increase in the sodium hydroxide part in the white liquor will lead to an increase of the formation of calcium carbonate in the green liquor, that by its time will demand more calcium hydroxide. The lime mud from the recausticizing stage, feeds the lime kiln. As a consequence of the sulfidity reduction, an increase in sodium hydroxide leads to a production of a greater amount of lime mud, that can surpass the lime kiln burning capacity.

Fig. 23. Effect of sulfidity on screened pulp yield, kappa number and viscosity for soda-0.04%DDA cookings (active alkali - 13% and H factor - 522)

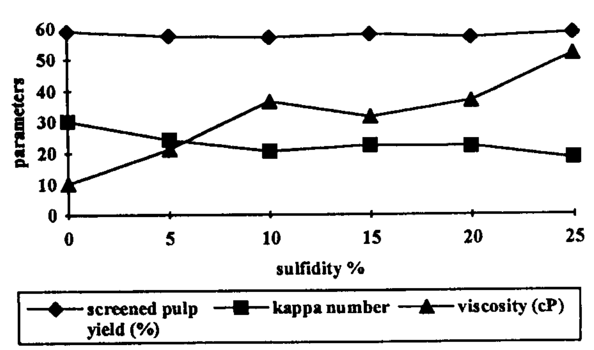
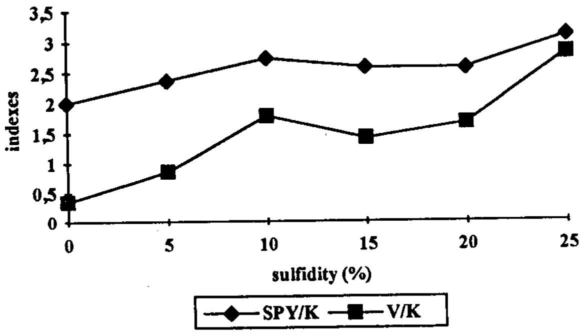


Figure 23 shows that sulfidity had no effect on the screened pulp yield. On the other hand, the effect of the sulfidity is clear in the reduction of kappa number and increase of pulp viscosity. This result shows the specificity of sodium sulfide for lignin degradation and that its use joined to DDA can be an effective alternative for pulp production.

Fig. 24. Effect of sulfidity on screened pulp yield (SPY)/kappa number (K) and viscosity (V)/kappa number (K) for soda-0.04%DDA cookings (active alkali - 13% and H factor - 522)



There is an increase in the screened pulp yield (SPY)/kappa number (K) and viscosity (V)/kappa number (K) indexes as a consequence of the reduction in kappa number and increase in pulp viscosity.

The sulfidity showed a good effect at levels between 5 and 10% for the pulping characteristics, specially kappa number and viscosity.

Also at this stage the soda pulp was inferior to the other pulps tested for strength properties

Fig 25. Effect of sulfidity on tensile index of soda-0.04%DDA pulps (active alkali - 13% and H factor 522)

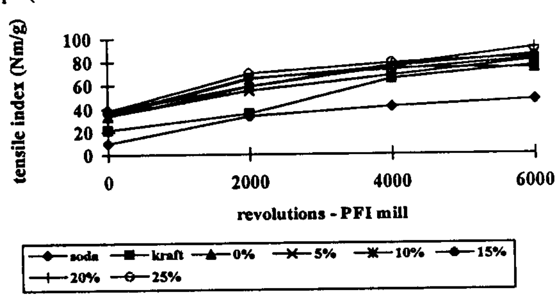


Fig. 26. Effect of sulfidity on burst index of soda-0.04%DDA pulps (active alkali - 13% and H factor 522)

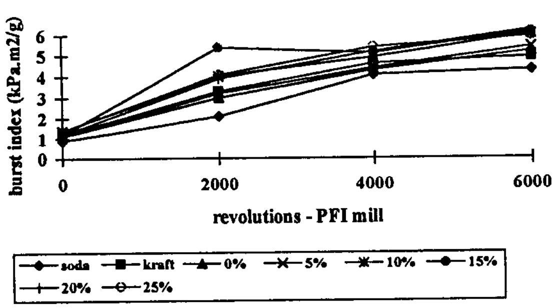


Fig. 27. Effect of sulfidity on tear index of soda-0.04%DDA pulps (active alkali - 13% and H factor - 522)

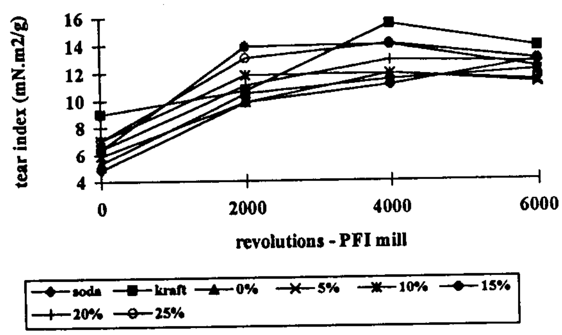
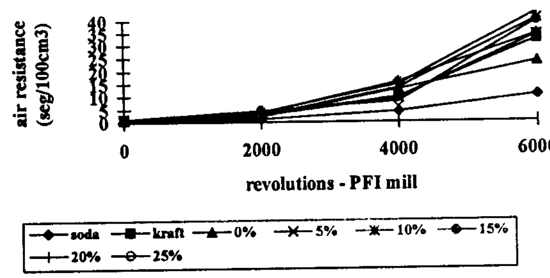


Fig. 28. Effect of sulfidity on air resistance of soda-0.04%DDA pulps (active alkali - 13% and H factor 522)



In these figures, it can be observed that the addition of sodium sulfide to soda-DDA cookings increase the air resistance, tensile and burst indexes of the pulps, when compared to traditional soda cooking, making the pulp very similar to a kraft pulp.

CONCLUSIONS

The addition of DDA to soda pulping process of *E. grandis* chips lead to the production of pulps with quality similar to kraft process.

Linking the technical aspects to the economic ones and considering the DDA charges tested in this research, for *E. grandis* soda-DDA pulping, the best charge of DDA is 0.04% (oven dry wood).

The use of 0.04% of DDA in soda cookings of *E. grandis* chips allow a reduction of approximately 7% on the active alkali (14 to 13%).

The use of 0.04% of DDA in soda cookings with 13% of active alkali of *E. grandis* chips allow the reduction of the H factor in approximately 23% without damage the pulp quality.

For the cooking conditions tested in this research the sulfidity between 5 and 10% allow the production of pulps with characteristics similar or superior to kraft pulps.

In kraft cooking the use of DDA allows the reduction of sulfidity in more than 60% without damage to the process yields and pulp quality.

DDA can be considered as a "process flexibilizer agent", because it shows effects over the pulping process, that can be explored individually, such as, the improvement of pulp quality, the increase of pulp yield, reduction of sulfidity, chemical and energy economy, among others.

LITERATURE CITED

1. Holton, H. H., *Pulp & Paper International*, "Better cooking with anthraquinone," 8:49-52 (1978).

2. Holton, H. H., *TAPPI Journal*, "AQ: unconventional thinking triumphs," 64(6):8-11(1981)

3. Blain, T. J., and Holton, H. H., *Pulp & Paper International*, "Economics of AQ pulping: The net value of increased production," 84(6):58-63 (1983).

4. Ghosh, K. L., Venkatesh, V., Chin, W. J., and Gratzl, J. S., *TAPPI Journal*, "Quinone additives in soda pulping of hardwoods," 60(11):127-131(1977).

5. Haldar, R., and Bhattacharya, P. K., *TAPPI Journal*, "Studies on kraft and soda-anthraquinone pulping of Indian mixed hardwoods," 7(6):129-132 (1987).

6. Biermann, C. J., and Dutta, T., *TAPPI Journal*, "Kraft cooking of Douglas-fir with 1,4-dihydro-9,10-dihydroxi anthracene," 72(2):175-177 (1989).

7. Kawasaki Kasei Chemicals Ltd, *Japan Pulp & Paper*, "Modern feature of cooking with quinone additive," 24(1):59-68 (1986).

8. Macleod, J. M., and Fleming, B. I., *TAPPI Journal*, "Delignification rates of alkaline-AQ processes," 66(12):81-82.

9. TAPPI Test Methods, TAPPI PRESS, Atlanta, 1988

10. Lima, A. F., Turquetti, A., Barreto, F., Ventura, J. W., and Silveira, P. R. P., "Antraquinona para redução das emissões de TRS: a experiência da Riocell," *XXVI Brazilian Pulp and Paper Congress Proceedings*, (1993).

ACKNOWLEDGMENT

The authors wish to thank São Paulo State Research Support Foundation for the financial support.