Modified kraft hardwood pulp yields high brightness and high strength

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ABSTRACT: The acute demand for high brightness is generating interest in the development of new pulping and bleaching technologies. The conventional hardwood kraft pulp (kappa 20) was found to be unsatisfactory largely due to its inability to meet the twin objectives of 90% ISO brightness and acceptable strength. These objectives can be achieved through modifications in the existing pulping and bleaching process. The use of kappa number 30 hardwood kraft pulp and extending the delignification by oxygen to a kappa number of 11 was found to be an effective way of achieving high brightness (90% ISO) with maximum cleanliness, at the same time maintaining the high strength properties. The performance of the modified pulping process was evaluated with various bleaching sequences for achieving high brightness and strength.

KEYWORDS: Bleaching, brightness, delignification, hardwoods, kappa number, kraft pulping, mechanical properties, modified kraft process, oxygen delignification, viscosity.

Tamil Nadu Newsprint and Papers Ltd (TNPL) is a large bagasse based integrated pulp and paper plant. The mill operates two different pulping lines, viz., bagasse kraft pulp and hardwood (eucalyptus hybrid) kraft pulp designed to produce 40,000 metric tons/year (mt/year) of printing and writing grades. The mill employs traditional CEHH bleaching sequence for conventional kappa 20 hardwood kraft pulp and CEH bleaching sequence for kappa 10 bagasse kraft pulp.

It has been standard practice to pulp hardwoods to a kappa number of 20 and then remove the remaining lignin in the subsequent conventional CEHH bleaching process. Pressure in the market has forced many mills to look for the most economical solutions to their pulping and bleaching problems. Technically, an elegant solution to these problems can be achieved by obtaining fully bleached brightness, acceptable strength and cleanliness using a minimum number of bleaching stages. There is an increased interest in the use of modern pulping and bleaching technologies to achieve the target goals in the advanced countries. These technologies will include both modifications to the existing technology and the development of new pulping and bleaching technologies, particularly for the softwood kraft pulp.

The two prominent commercial new pulping technologies available are:

- Rapid heat displacement (RDH) *(1, 2)*
- Modified continuous cooking (MCC) *(3, 4)*.

The current trend in bleaching technology is to achieve high brightness through total chlorine free bleaching (TCF) or elemental chlorine free bleaching (ECF). Therefore, the current driving force in the use of high brightness is environmentally friendly bleaching technologies. These include the introduction of oxygen *(5, 6)*, hydrogen peroxide *(7, 8)*, ozone *(9, 10)*, and chlorine dioxide *(11, 12)* in a multi-stage bleaching sequence. These applications enhance the effectiveness beyond the conventional improvements in brightness and strength characteristics.

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These newer pulping and bleaching processes are very promising and have been adopted by advanced countries. While these technologies are interesting in such countries, they are of less practical significance in the developing countries where the conventional hardwood pulp is still bleached with traditional first stage chlorine in the multistage bleaching.

The conventional CEHH bleaching sequence for hardwood kraft now being practiced in our plant brings up the brightness only to a level of 80% ISO. Further enhancement in the brightness of the hardwood kraft by the conventional bleaching sequence results in the usage of excessive bleaching chemicals such as chlorine and calcium hypochlorite, and thus results in poor pulp quality.

In order to extend product diversification, and to compete with the high-quality products in the market, a high brightness hardwood kraft pulp (85–90% ISO) with acceptable strength and cleanliness is warranted in the present furnish. The development of these products can be achieved only by improving existing pulping technology and bleaching procedures.

The main objective, therefore, was to evaluate a modified pulping process and bleaching method for hardwood kraft pulp, which can enhance the brightness to 85–90% ISO with good strength and a moderate retrofitability in the existing plant. These applications include raising the hardwood kraft pulp kappa number to 30 and to extend delignification by oxygen and compare results with conventional hardwood kraft pulp of kappa number 20 in terms of pulp strength and pulp bleachability. This is one of the several approaches planned to identify and apply new pulping and bleaching technologies in process control to improve the pulp and paper products.

I. Pulping conditions for conventional kraft pulp (kappa 20) and modified kraft pulp (kappa 30)

Parameters	*Conventional kraft pulp*	*Modified kraft pulp*
Raw material per charge,kg (o.d.)	1.5	1.5
Wood-to-liquor ratio	1 : 2.8	1 : 2.8
Cooking temperature, °C	170	170
Cooking time, min	90	90
Chemical charge, %	15	13
H factor	1600	1600

II. Unbleached pulp characteristics of conventional kraft pulp and modified kraft pulp

Characteristic	*Conventional kraft pulp*	*Modified kraft pulp*
Kappa number	20.0	30.0
Brightness, % ISO	23.9	21.7
Viscosity, cP	10.5	18.4

Experimental

Bleaching experiments were carried out using an unbleached hardwood (eucalyptus hybrid) kraft pulp. Two different pulps, one with conventional kappa 20 and the other pulp of modified kappa 30, were selected for these studies. The conventional kraft pulp kappa 20 was produced from our existing pulp mill while modified kraft pulp kappa 30 was produced in the laboratory by the 18-L capacity electrically heated programmable rotating digester. The pulping conditions maintained for the both conventional and modified kappa pulps are given in **Table I**, and the characteristics of the unbleached pulps are shown in **Table II**.

Oxygen delignification (O) and oxidative extraction [E(O)] were simulated in the same laboratory programmable rotating digester using 500 g o.d. pulp. 0.5% $MgCO_3$ was added in both oxygen delignification and oxidative extraction stages to protect the pulp viscosity of 6 cP. The optimization of chlorine in the chlorination stage was carried out in plastic containers using 20 g o.d. pulp. Chlorine was applied as multiples of kappa number XO.11, XO.14, XO.17, XO.20, XO.23%. The optimum chlorine dosage was determined by plotting chlorine percent applied against residual chlorine. The corresponding chlorine dosage at the point of inflexion of the curve decides the optimum chlorine requirement. Standard runs were carried out in plastic containers with 200 g o.d. pulp using optimized chlorine dosage.

Optimization of the extraction stage was carried out in sealed polyethylene bags with different dosages of sodium hydroxide and the minimum dosage corresponding to a final pH of >10.5 was chosen as the optimum.

III. Bleaching conditions

Conditions	O	E(O)	D	C	E	H
Consistency, %	12	12	8	3	8	8
O_2 pressure, kg/cm^2	7.0	5.0	--	--	--	
Temperature, °C	120	100	70	Ambient	60	40
Reaction time, min	60	30	180	30	60	120
Final pH	>10.5	>10.5	5.5-4.5	2.0-3.0	>10.5	9.5-8.5
Cl_2, %	--	--	--	1.8-4.0	--	--
ClO_2 as Cl_2, %	--	0.5-2.0	--	--	--	--
NaOH, %	2.0-2.5	1.5-2.0	--	--	0.8-2.0	--
Calcium hypochlorite as Cl_2, %	--	--	--	--	--	0.5-1.6

IV. Bleaching characteristics of conventional kraft pulp (kappa 20) under optimized conditions

Sequence	Viscosity, cP	Brightness ISO, %	Post color number	Scattering coeff., m^2/kg	Total active chlorine, %	Total alkali, %
C E H H	5.3	80.0	2.53	61.1	4.83	1.83
C E (O) H H	4.8	84.5	1.16	62.1	4.79	1.70
C E (O) H D	5.2	86.0	0.84	62.6	5.10	1.60
C E (O) H E D	4.9	86.8	0.72	61.8	5.12	1.93
C E (O) D E D	6.4	87.7	0.65	62.8	5.99	1.87
O C E H E D	4.9	87.0	0.68	60.4	2.30	2.78
O C E D E D	5.3	89.0	0.62	59.0	2.12	2.80

Calcium hypochlorite dosage was optimized so as to achieve 80% ISO final brightness in the conventional CEHH sequence. Chlorine dioxide solutions for bleaching experiments were prepared in our laboratory. The chlorine dioxide bleaching was performed in sealed polyethlylene bags. Laboratory conditions maintained for the various stages of the bleaching sequences are shown in **Table III.**

Analysis

The pulp kappa number, viscosity, strength properties, and post color number were evaluated as described in TAPPI Methods T 236, T 230, T 220, T 260, respectively. Brightness, post color number, and scattering coefficient were measured using the Elrepho-Mat Datacolor brightness tester.

Results and discussion

Conventional hardwood kraft pulp (kappa 20)

Our plant hardwood pulp production line consists of four-stage conventional CEHH bleaching to attain final brightness of 80% ISO for the kraft pulp. The existing bleaching sequence has to be partially modified to reach high brightness while maintaining the acceptable pulp quality. Therefore, an extensive laboratory evaluation program was first initiated to identify a suitable bleaching sequence easily adaptable in the existing bleach plant without changing the characteristics of the pulp. This task was accomplished by introducing oxygen and chlorine dioxide stage along with four stage CEHH bleaching. Various alternative bleaching sequences combining with oxygen and chlorine dioxide were studied.

Bleaching sequences were selected to produce pulp with brightness of 85–90% ISO when the target brightness was 85% ISO, a simple bleaching sequence consisting of four stages combining with reinforced oxidative extraction [E(O)] was employed. On the other hand, when the brightness requirement was 90% ISO, oxygen delignification followed by a five-stage bleaching sequence was adopted.

The criteria used for determining the performance of these bleaching sequences were the brightness gain and strength properties of the handsheets produced. To compare the performance of various sequences used, we chose the conventional CEHH bleaching sequence of 80% ISO brightness as a reference point.

Table IV summarizes the bleachability of conventional kraft pulp (kappa 20) with different bleaching sequences. It has been shown that the first target brightness of 85% ISO is easily achievable for the conventional pulp by short bleaching sequence of CE(O)HH or CE(O)HD. Adding 0.5% of chlorine dioxide (as Cl_2) as a final D stage in place of H in the above sequence was particularly advantageous in terms of final brightness gain and color reversion.

Although the brightness of 85% ISO was easily achievable with the conventional kraft pulp, the bleaching sequences including the oxidative extraction with an additional dioxide and extraction stages [CE(O)DED] could reach 88% ISO only. Interestingly, the 89.0% ISO brightness was achieved with the sequence OCEDED, indicating an apparent synergetic effect between oxygen delignification and chlorine dioxide in the final bleaching stages.

The maximum achievable brightness in the chlorine dioxide stage is largely determined by the kappa number of the incoming pulp. Carmichael *et al.* *(13)* reported that a final brightness of 90% ISO with chlorine dioxide can be achieved only if the pulp at the beginning of the D stage has a kappa number of 2 or less. As we have stated that pulp with a final brightness of 90% ISO is one of our objectives, efforts were made in this bleaching sequence to minimize the kappa number leaving the extraction stage below 2.0. An alternative approach proposed for this purpose was to use oxygen delignification for the conventional kappa pulp before the bleaching sequence. Following oxygen delignification, the conventional kraft hardwood unbleached pulp of 20 kappa number had a kappa number of 1.8 before entering into the first D stage. It is to be noted that oxidative extraction [E(O)] had little effect on the kappa number reduction *(14)*, and thus resulted in the ceiling of final brightness at 87.7% ISO for the sequence CE(O)DED compared to OCEDED.

V. Strength properties of conventional kraft pulp (kappa 20) evaluated at 300 mL CSF

Sequence	*Tensile index, Nm/g*	*Tear index, mN·m²/g*	*Burst index, kPa·m²/g*
C E H H	73.5	7.14	4.50
C E (O) H H	70.0	7.10	4.15
C E (O) H D	61.0	6.35	3.90
C E (O) H E D	56.5	5.60	3.25
C E (O) D E D	58.5	5.90	3.40
O C E H E D	58.8	7.06	3.92
O C E D E D	49.3	6.05	2.55

VI. Bleaching characteristics of modified kraft pulp (kappa 30) under optimized conditions

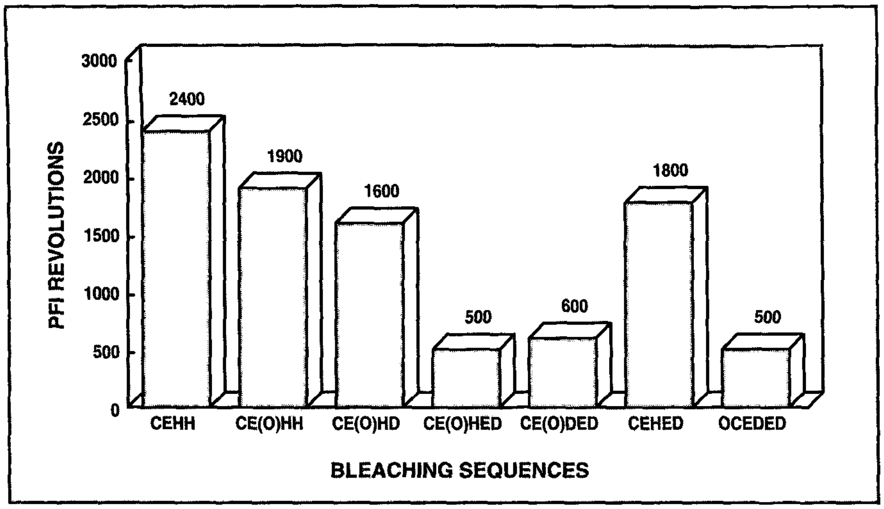
Sequence	*Viscosity, cP %*	*Brightness ISO, number*	*Post color m²/kg*	*Scattering coeff., chlorine,*	*Total active % %*	*Total alkali*
C E H H	6.5	80.0	2.09	57.5	5.73	1.96
C E (O) H H	6.5	85.7	1.11	57.4	5.14	1.88
C E (O) H D	7.3	87.4	0.63	57.5	5.47	1.93
C E (O) H E D	5.3	88.3	0.43	57.5	6.04	2.23
C E (O) D E D	10.1	90.7	0.31	60.3	7.10	2.30
O C E H E D	6.4	90.8	0.35	59.2	2.44	3.19
O C E D E D	8.3	91.1	0.29	59.5	2.49	3.07

VII. Strength properties of modified kraft pulp (kappa 30) evaluated at 300 mL CSF

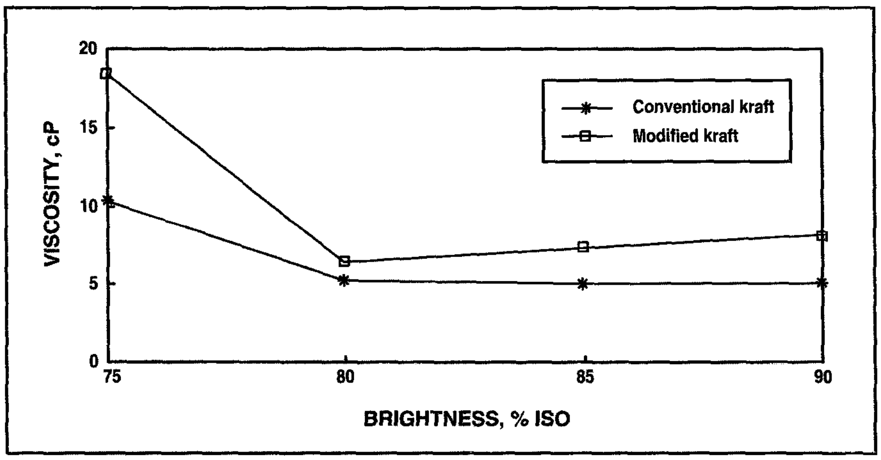
Sequence	*Tensile index, Nm/g*	*Tear index, mN·m²/g*	*Burst index, kPa·m²/g*
C E H	76.0	7.80	5.30
C E(O)H H	74.0	8.10	4.70
C E(O))H D	63.0	7.50	4.00
C E(O)H E D	80.5	6.80	5.35
C E(O)D E D	82.5	8.50	5.65
O C E H E D	67.0	7.30	4.05
O C E D E D	67.0	7.80	5.30

With respect to the chlorine consumption, bleaching sequences following oxygen delignification required less chlorine than the ones that incorporated oxygen in the extraction stage. The OCEDED

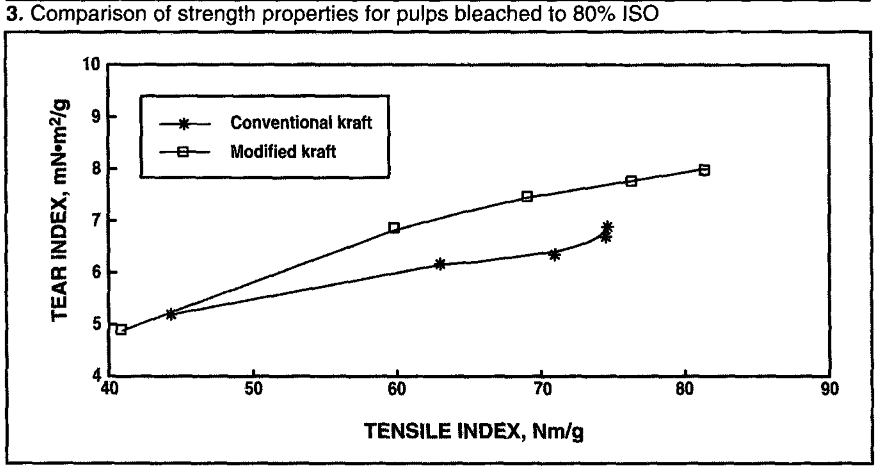
1. Beating characteristics for fully bleached conventional kraft pulps at 300 mL CSF



2. Viscosity vs. brightness for fully bleached pulps



3. Comparison of strength properties for pulps bleached to 80% ISO



bleached pulp with high brightness showed a drop of 65% in active chlorine consumption than those for CE(O)DED bleached pulp. The pulps bleached with both the sequences CE(O)DED (87.7% ISO brightness) and OCEDED (89.9% ISO brightness) showed good light scattering properties (Table IV).

Viscosity and physical strength of various bleaching sequences using the conventional kraft pulp were evaluated. Taking the average viscosity of the CEHH as a basis for comparison, viscosity was not affected to any significant degree by the oxygen and chlorine dioxide stages (Table IV). This behavior was maintained throughout all six phases of the bleaching sequences.

However, the improvement in viscosity was not reflected in better physical strength of the refined bleached pulps at 300 mL CSF. All bleaching sequences tended to have a lower tensile index, tear index, and burst index when compared to the reference CEHH sequence (**Table V**). It can also be observed that, among the bleaching sequences, the pulp bleached with OCEDED, which gave higher brightness, suffered significant damage in strength properties. It appears that oxygen delignification of conventional kraft pulp (kappa 20) was considerably detrimental to the carbohydrates, resulting in poor pulp strength.

The lower beating requirement of the fully bleached pulps (**Fig. 1**) probably reflects more cellulose degradation, as indicated by the poor strength properties of the pulps.

From the foregoing discussion, we conclude that it is difficult to bleach the conventional hardwood kraft pulp (kappa 20) to the target brightness (90% ISO) with acceptable strength properties.

Obviously, a strong unbleached hardwood pulp to achieve the target goals of high brightness and high strength is warranted. In conventional kraft pulping, the hardwood kappa number was limited to 20 in order to avoid the severe loss in pulp strength. Plant hardwood pulp produced under standard conditions at kappa number 20 still had a low starting viscosity (10.5 cP). Such pulps exhibit poorer strength properties than pulps delignified in the oxygen stage to the same kappa number *(5)*.

A brightness up to 84–86% ISO is not too difficult to achieve. However, to produce market pulp of over 90% ISO required additional efforts in each stage of the whole fiber line, from cooking to final bleaching. To do this, it became clear that a better starting point was necessary for entering into the bleaching process. The unbleached kappa number of the pulp would need to be decreased to new, lower levels, while at the same time maintaining or enhancing the quality of the unbleached pulp. This was accomplished by extended delignification in the pulping step.

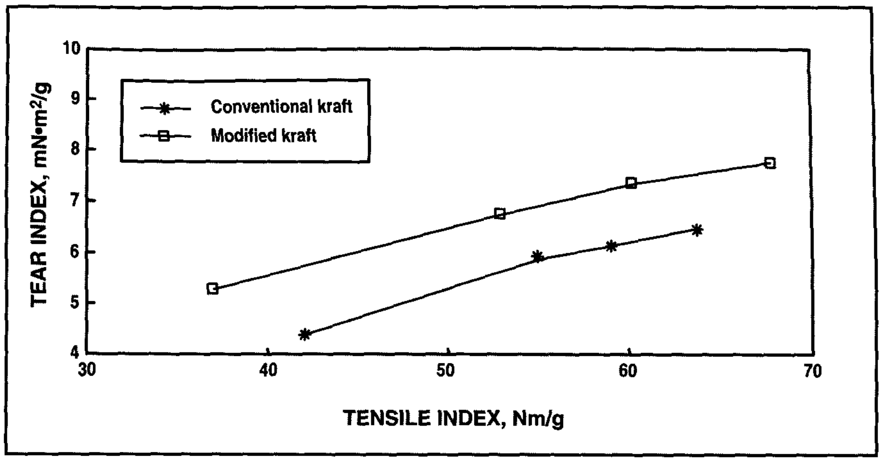
Consequently, modifications to the existing hardwood kraft pulping process have been aimed at raising the kappa number of the unbleached pulp to 30 and extend delignification through oxygen without a severe loss in pulp strength. The proposed process is simple to implement in an existing mill, and incorporates the above principles.

Modified hardwood kraft pulp (kappa 30)

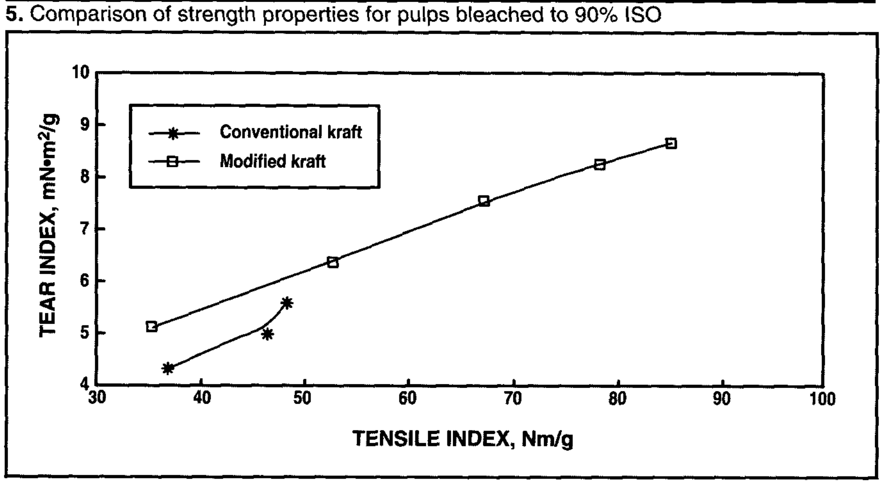
A modified unbleached kraft hardwood pulp (kappa 30) was oxygen delignified to kappa number 11 and bleached with similar sequences, as in the case of conventional kraft hardwood (kappa 20).

The characteristics of modified kraft pulp bleached under optimized conditions are presented in **Table VI**. The results demonstrate a significant difference in bleachability between modified kraft pulp and conventional kraft pulp. The bleachability of modified kraft pulp was consistently higher than that of conventional kraft bleached pulp for the same final bleaching sequence. A brightness of over 91% ISO could be easily achieved for the sequence OCEDED. The brightness ceiling was about 3–4 units higher for the modified kraft pulp compared to conventional kraft pulp in the corresponding bleaching sequences.

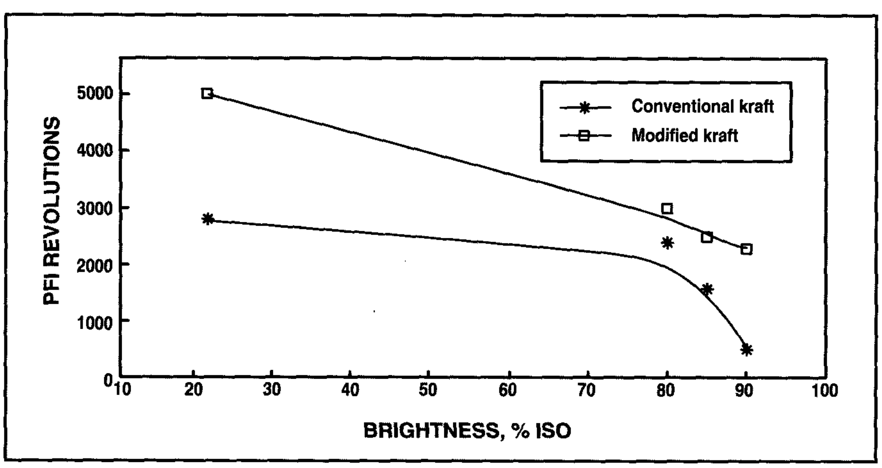
4. Comparison of strength properties for pulps bleached to 85% ISO



5. Comparison of strength properties for pulps bleached to 90% ISO



6. Beating characteristics for fully bleached pulps at 300 mL CSF



It is obvious that the performance of the modified kraft cooking process has a significant effect on improving the bleachability of the pulp. The strength indexes of fully bleached modified kraft cooking pulps increased roughly to the extent of reference pulp. The tear resistance continued to increase with refining down to 300 mL CSF (**Table VII**). Although the tearing strength developed in the same way for all bleaching sequences, the tensile strength was slightly lower than the reference pulp. The higher tear resistance and higher viscosity of the bleached pulps suggest the selectivity of the modified kraft cooking by enhancing delignification.

Modified hardwood kraft pulp vs conventional hardwood kraft pulp

1. The possibility of increasing hardwood unbleached kraft pulp kappa number to 30 and extending the delignification to kappa number 11 by first-stage oxygen was found to be an effective way of achieving high brightness (90% ISO) with maximum cleanliness, while maintaining the high-strength properties.

2. Pulp viscosity as a measure of final pulp strength was found to be higher for modified kraft pulps than the conventional kraft pulps at different brightness levels (**Fig. 2**).

3. Another interesting trend observed is that the modified kraft bleached pulps retain their strength properties (Table VII). Modified kraft bleached pulps are consistently trending stronger than their conventional counterparts. The improvement in the pulp properties after final bleaching stages should be interpreted with respect to the properties of the unbleached pulp, which had a high starting viscosity (18.4 cP).

   According to Rydholm *(15)* and MacLeod *(16)* tear–tensile relationships provide a valid basis for comparing the strength of the pulps obtained by applying different pulping or bleaching procedures. These relationships are presented in **Figs. 3 through 5.**

   At a given tensile index value of 60 Nm/g, at which the tearing strength of modified kraft pulp bleached to 85–90% ISO brightness showed about 15% higher than the conventional kraft pulps. The gain in sheet strength can be attributed to the higher viscosity of the bleached pulp.

4. The introduction of oxygen delignification in the modified kraft pulping process has been driven by environmental, economic and energy related considerations *(17, 18)*. The reduction of the kappa number in the pulp going to chlorination affects linearly the effluent chemical oxygen demand (COD) and adsorbable organic halides (AOX). Total active chlorine consumption depends linearly on the kappa number *(5)*.

5. The modified hardwood kraft pulping process can offer significant savings in chemical cost arising from reductions in the need for chlorine and chlorine dioxide. Chlorine dioxide savings in the later stages are presumed to be due to beneficial changes in the residual lignin structure brought about by its earlier exposure to oxygen (Table VI).

6. The beating energy (PFI revolutions) requirement of modified kraft pulp was higher than the conventional kraft pulp (**Fig. 6**), indicating that unwanted attack on the carbohydrate was avoided in the modified pulping process. This demonstrates the principal reason for extending the delignification prior to bleaching.

7. Considering the results of the experiments given in this paper, it can be stated that incorporation of oxygen delignification to the 30 kappa hardwood kraft pulp followed by the five-stage CEHED or CEDED bleaching sequence could lead to a final brightness of 90% ISO without impairing the pulp strength. **TJ**

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Received for review June 6, 1993.

Accepted Oct. 7, 1993.