High-kappa pulping and extended oxygen delignification decreases recovery cycle load

Brijender Parsad, Josef Gratzl, Adrianna Kirkman, Hasan Jameel, Thomas Rost, and Vincent Magnotta

ABSTRACT: It is well established that the removal of lignin by an oxygen/alkali treatment is more selective than by conventional pulping. The aim of this study was to evaluate the feasibility of pulping to kappa numbers ranging from 30 to 60, followed by one or two oxygen stages to lower the lignin content of the pulps entering the bleach plant and at the same time to minimize the load to the boiler. Computer-aided process simulation of the mill, using GEMS, was carried out for all the cases. By pulping to a kappa number of 40, followed by two-stage oxygen treatment [40(OO)] to kappa 13, the load to the recovery boiler is lower than in the base case—pulping to kappa 30. In addition, operating costs and pollution potential of the fully bleached pulps by a conventional sequence (DEopD) were lower when compared to the base case. Even lower loading to the boiler could be achieved if the pulping is terminated at kappa number 50 and followed by two-stage oxygen delignification [50(OO)].

KEYWORDS: Alkali treatment, alkaline pulping, bleaching, chemical pulping, chemical reactions, chemical treatment, computer programs, delignification, economics, evaluation, kappa number, kraft pulping, mechanical properties, multistage process, nonmetals, oxygen, permanganate number, recovering, simulation, technology, two stage process.

Environmental concerns in the paper industry have led to a need to reduce the kappa number of pulps entering the bleach plant in order to reduce the BOD and AOX of the effluent discharged. There are essentially two ways to achieve the goal of extended delignification prior to the bleach plant:

1. Use modified kraft pulping with liquor profiling in a continuous digester or with liquor pretreatments in a batch digester.
2. Use an oxygen stage following kraft pulping.

A major drawback of both options is that an increase in the load to the recovery boiler can be expected. However, an extended oxygen delignification (EOD) system, which requires pulping to a higher kappa number (35–65) followed by oxygen delignification, has been found to be more yield selective than kraft pulping *(1)*. Since oxygen delignification is more yield selective than pulping, it should be possible to decrease the organics to the recovery system by properly selecting the kraft kappa number and two-stage oxygen conditions.

In addition to minimizing additional recovery load and reducing environmental impact, other issues of concern with this approach to extended delignification are pulp quality (strength properties) and process economics. Therefore, studies were undertaken with the following objectives:

- Evaluate the effect of two-stage oxygen delignification of pulps in the 30–60 kappa number range on recovery.
- Examine the economics of such processes with respect to pollution load.

All authors except Magnotta work for the Department of Wood and Paper Science at North Carolina State University, Raleigh, NC 27695. Magnotta is with Air Products and Chemicals Inc., 7201 Hamilton Blvd., Allentown, PA 18195-1501.

I. Bleaching conditions

Sequence	Stage	Consistency, %	Temperature, °C	Time, min	Pressure, psi	Charges, %
ECF	D1	3.5	50	60	Atms	0.22 kappa, 100% subs.
	Eop	10	70	60	30	0.6% Cl_2 charge 0.25% H_2O_2
	D2	10	70	180	Atms	1.0% ClO_2
TCF	Z1	10	40	1	Atms	0.75% Ozone
	Eop	10	70	60	30	3% Alkali 0.25% H_2O_2
	Z2	10	40	1	Atms	0.52% Ozone
	P	10	70	120	Atms	2% Peroxide

- Compare the strength properties of such pulps with conventional kraft or kraft oxygen delignified pulps.

This study is divided into two parts. The first part includes the experiments carried out in the laboratory to obtain the data for the computer simulation and the evaluation of strength properties of the different pulps after bleaching. The objective of the second part is to use the data obtained from the experiments in a full mill simulation for technical and economic evaluation of selected delignification sequences followed by either elemental chlorine-free (ECF) or total chlorine-free (TCF) bleaching sequences.

II. Pulping optimization

Cook no.	Active alkali, %	H factor	Total yield, %	Screened yield, %	Rejects %	Kappa number
1	16	800	53.9	42.2	11.5	62.0
2	16	1100	49.1	43.8	5.3	50.1
3	16	1400	48.3	44.6	3.7	41.4
4	16	1700	45.6	43.2	2.4	33.8
5	18	800	48.3	44.3	4.0	49.2
6	18	1100	46.2	44.7	1.5	36.9
7	18	1400	45.0	44.0	1.0	29.9
8	18	1700	44.5	43.9	0.6	26.0
9	20	800	45.4	43.5	1.9	40.1
10	20	1100	42.9	42.0	0.7	30.2
11	20	1400	42.2	41.5	0.7	25.0
12	20	1700	41.2	40.8	0.4	20.9

Experimental

Pulping optimization

The purpose of this series of experiments was to identify the conditions necessary to reach kappa numbers 40, 50, and 60. Pulping of southern pine chips was carried out in a M&K digester (seven liter capacity) at four different H-factors and three different active alkali charges, keeping sulfidity constant at 25%. Active alkali charges used were 16%, 18%, and 20% at H-factors of 800, 1100, 1400, and 1700. Kappa number, yield, and rejects were measured in each case.

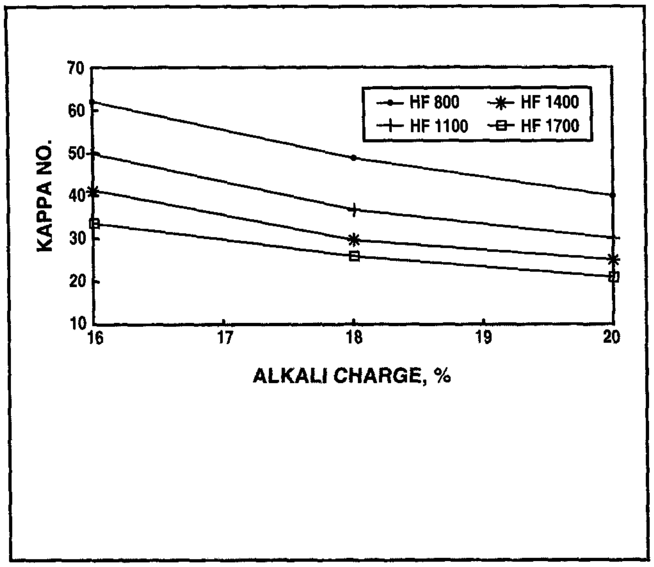
Rejects study

One concern of particular interest in high-kappa pulping is the higher amount of rejects generated. Reduction of the rejects is possible if the rejects are sent to the oxygen delignification stages and if screening is done after the oxygen washers. The effect of oxygen delignification on the rejects was studied for two pulps (with kappa numbers 40 and 50) prepared in the M&K digester. Both of the pulps were washed and divided into three parts. The first part was screened, and the OD weight of rejects was measured. The remaining two parts were subjected to one- and two-stage oxygen delignification at 3% alkali charge, 100°C temperature, and 100 psi pressure. The oxygen delignified pulps were screened, and the rejects were measured in each case.

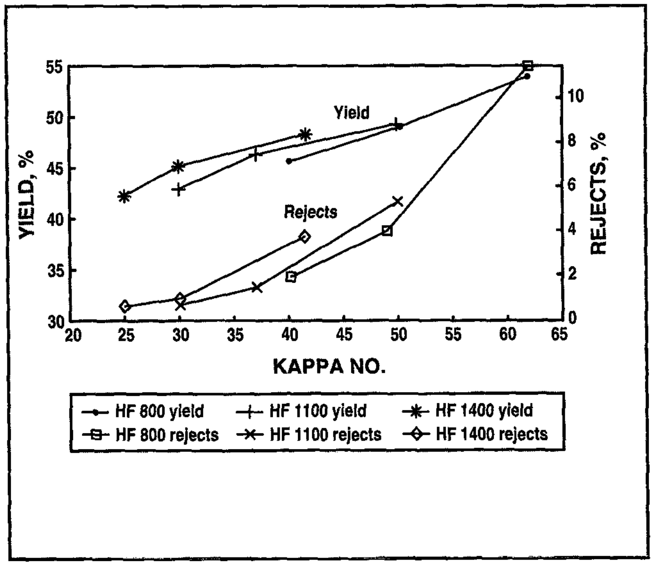
Oxygen delignification

The objective here was to optimize one- and two-stage oxygen delign-

1. Alkali charge vs. kappa number



2. Yield and rejects vs. kappa number



III. Rejects study

Kappa	*Stages*	*Rejects, %*	*Reduction, %*
	Pulping	3.1	...
40	One-stage	0.7	77
	Two-stage	0.1	96
	Pulping	7.8	...
50	One-stage	1.5	80
	Two-stage	1.3	84

ification and to examine the effect of interstage washing between two stages of oxygen delignification. Oxygen delignification of softwood pulps was carried out in a high-shear mixer (Quantum reactor MK II) at 100 psi, 100°C, 10% consistency, and 0.5% magnesium sulfate for one hour. Oxidized white liquor (sulfide oxidized to sulfate) was used as the alkali source for all experiments. One- and two-stage oxygen delignification of four different pulps with kappa numbers 30, 40, 50, and 60, with and without interstage washing, were studied under these conditions.

Bleaching

An elemental-chlorine-free sequence (DEopD) and a total-chlorine-free sequence (ZEopZP) were used for bleaching to a brightness ranging from 84% to 87% ISO. The conditions are listed in **Table I**. Strength properties were measured according to TAPPI methods. Yield, brightness, and strength properties of the bleached pulp were determined. The yield data were used for the simulation.

Results

Pulping

The pulping results are summarized in **Table II. Figure 1** shows the kappa numbers achieved at different alkali charges at a constant H-factor (HF). Optimum conditions to reach a kappa number of 30 are an active alkali of 19.8% as Na_2O and H-factor 1100, based on relatively low rejects and moderately higher yields, as shown in **Figs. 1 and 2**. From a baseline kappa number of 30 (active alkali 20% and H-factor 1100), higher kappa numbers of 40 and 50 can be achieved by decreasing either active alkali or H-factor. For the simulation, pulps with kappa numbers of 40 and 50 were prepared by decreasing the active alkali and keeping the H-factor constant at 1100. Thus, the production rate will not change from one case to another. Active alkali charges selected for kappa 30, 40, and 50 are as follows: kappa 30 = 19.8%, kappa 40 = 17.8%, kappa 50 = 15.8%.

Rejects

The reduction in the rejects that can be achieved by one- and two-stage oxygen delignification for kappa numbers 40 and 50 are shown in

Table III. For the process simulation, described in the next section, a 75% reduction in rejects in the first and a 25% reduction in the second oxygen delignification stage were assumed.

Oxygen delignification

Figure 3 shows the percentage delignification at different alkali charges during an oxygen stage. Results of the alkali charge optimization experiments are shown in **Table IV**. Increasing the alkali charge from 2% to 3% results in a substantial increase in delignification and brightness. The gains in delignification and brightness are much lower by increasing the alkali charge from 3% to 4%. A 3% alkali charge was chosen for further oxygen delignification experiments.

Results for one- and two-stage oxygen delignification with and without interstage washing are shown in **Table V** and in **Figs. 4 and 5**. Delignification and brightness are lower with washing between the two oxygen stages than for those without interstage washing. Higher delignification in the cases without interstage washing may be due to the residual alkali present in the system, which increases the total alkali concentration in the beginning of the second oxygen stage. This is further confirmed by the higher pH at the end of the second oxygen delignification stage. In addition, a brightness improvement of about 2% was observed. However, the viscosities are significantly lower in pulps produced in experiments without interstage washing, as shown in Fig. 5. Yields are comparable in the two cases.

Bleaching

Yields and brightness results for selected pulps are shown in **Table VI**. For ECF sequences, the brightness of the bleached pulp increases with decreasing kappa number to the bleach plant. Brightness is within the target brightness range of 83%

IV. One-stage oxygen delignification

Charge, %	*Final kappa no.*	*Delignification, %*	*Brightness, % ISO*	*Viscosity, mPas*
2	21.3	41	26.6	24.2
3	17.2	52	29.1	20.2
4	15.3	58	29.5	18.4

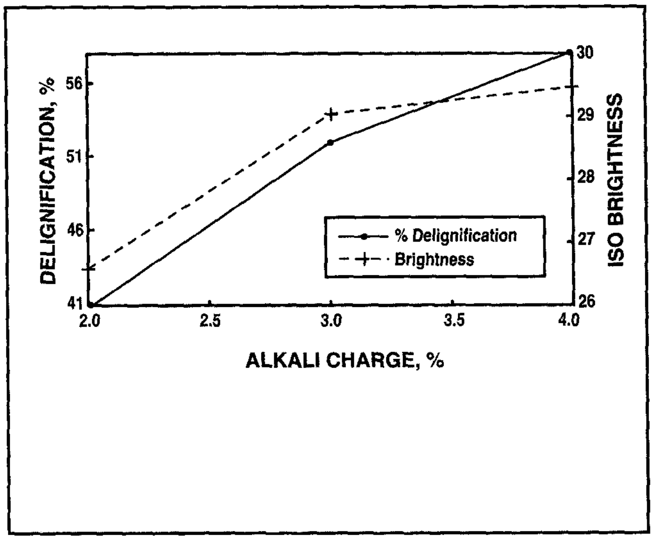
Initial kappa of the pulp was 36.
Temperature = 100°C. Pressure = 100 psi. Time = 60 min.

V. Two-stage oxygen delignification

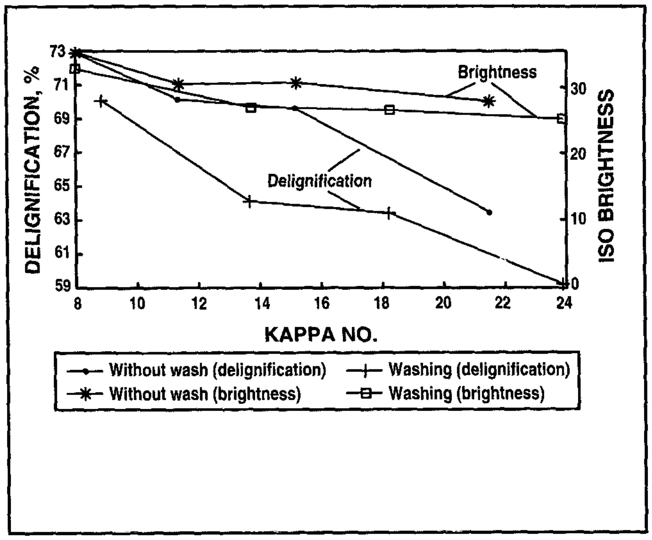
				Two-stage	
Parameter	*Cases*	*Initial values*	*One-stage*	*With washing (O)(O)*	*Without washing (OO)*
Final kappa	Kappa 30	29.4	13.0	8.8	8.0
	Kappa 40	38.1	18.0	13.7	11.4
	Kappa 50	49.9	24.9	18.3	15.2
	Kappa 60	58.7	35.6	24.0	21.6
Viscosity, mPas	Kappa 30	22.9	17.3	14.4	11.6
	Kappa 40	34.1	25.1	21.9	16.4
	Kappa 50	39.1	28.7	21.7	17.0
	Kappa 60	41.6	29.1	22.5	20.0
Brightness, % ISO	Kappa 30	25.6	30.1	33.3	35.5
	Kappa 40	23.0	24.2	27.2	31.0
	Kappa 50	22.0	24.3	26.8	31.0
	Kappa 60	20.2	22.8	25.3	27.9
Delignification, %	Kappa 30	...	55.8	70.1	72.8
	Kappa 40	...	52.7	64.0	70.1
	Kappa 50	...	50.0	63.3	69.5
	Kappa 60	...	39.3	59.2	63.3
Yield, %	Kappa 30	...	97.2	96.4	96.1
	Kappa 40	...	96.2	95.5	95.1
	Kappa 50	...	95.8	94.7	93.8
	Kappa 60	...	95.2	92.5	92.1
End pH	Kappa 30	...	11.1	10.9	11.7
	Kappa 40	...	10.6	11.8	12.3
	Kappa 50	...	10.3	11.3	11.9
	Kappa 60	...	10.0	10.5	11.7

Temperature = 100°C. Pressure = 100 psi. Time = 60 min. Alkali = 3%.

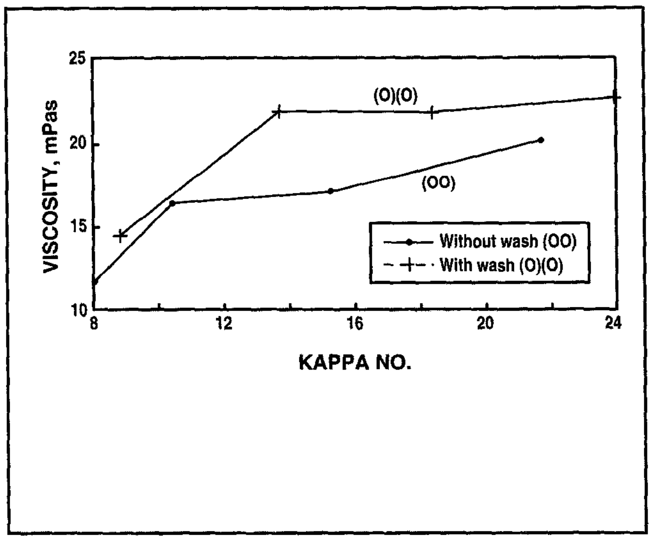
3. Single-stage oxygen delignification



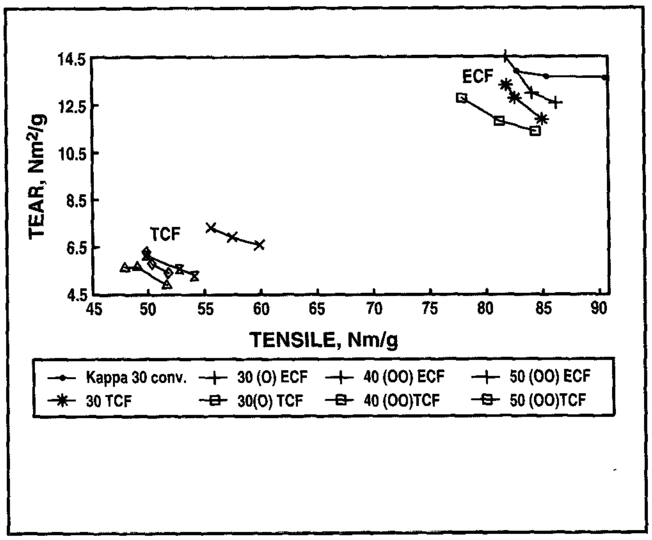
4. Two-stage oxygen delignification



5. Kappa number vs. viscosity (two-stage oxygen delignification)



6. Tear vs. tensile



to 87% ISO for all of the cases, except for conventional 30-kappa pulp without oxygen delignification for the TCF bleaching sequence. Therefore, this case was not included in the simulation study. Yields for all the other cases were used for the simulation study. Yields for ECF sequences are higher than their corresponding TCF sequences.

Strength properties

Tensile and tear of ECF and TCF pulps are compared in **Fig. 6**. For ECF pulps, tear and tensile of one-stage oxygen delignified pulp, 30(O) ECF, is lower than the conventional 30-kappa pulp. The strength properties for 40(OO)-ECF and 50(OO)-ECF pulps are lower than one-stage oxygen pulp [30(O) ECF]. The tear and tensile of 40(OO)-ECF pulp is lower than the conventional 30-kappa pulp at the same freeness of 390 CSF by about 3.6% and 6.7%, respectively. Kappa 40 pulp with two-stage oxygen delignification has better tear and tensile than the kappa 50 pulp with two-stage oxygen delignification for ECF sequences.

Tear and tensile of TCF pulps are significantly lower than the ECF pulps, which may be a result of relatively higher dosages of ozone in the TCF sequence. A significant decrease in strength properties is noticed for the 30-TCF pulp as compared to the 30-ECF pulp. An incremental loss in strength properties was also observed for both one- and two-stage oxygen delignified TCF pulps compared to ECF pulps. However, there is no significant difference in strength properties of one-stage oxygen delignified pulp of

VI. Bleaching of southern pine kraft pulps

(ECF and TCF sequences)

Cases	*Sequences*	*Kappa to bleach plant*	*Yield, %*	*Brightness, % ISO*
30 ECF	DEopD	29.8	92.4	83.5
30(O) ECF	DEopD	15.5	95.2	85
40(OO) ECF	DEopD	12.9	95.5	86
50(OO) ECF	DEopD	17.2	94.9	84
30 TCF	ZEopZP	29.8	91.7	70
30(O) TCF	ZEopZP	15.5	92.0	86
40(OO) TCF	ZEopZP	12.9	91.8	87
50(OO) TCF	ZEopZP	17.2	92.4	87

VII. Simulation cases

Initial simulation cases ⇒	Selected cases (final simulation)
Kappa 30 + no oxygen (conventional)	Kappa 30 + no oxygen (conventional)
Kappa 30 + one oxygen stage	Kappa 30 + one oxygen
Kappa 30 + two oxygen stages	Kappa 40 + two oxygen
Kappa 40 + one oxygen stage	Kappa 50 + two oxygen
Kappa 40 + two oxygen stages	
Kappa 50 + one oxygen stage	
Kappa 50 + two oxygen stages	
Kappa 60 + one oxygen stage	
Kappa 60 + two oxygen stages	

kappa 30 and two-stage oxygen delignified pulps of kappa numbers 40 and 50 bleached by TCF sequences.

Simulation studies

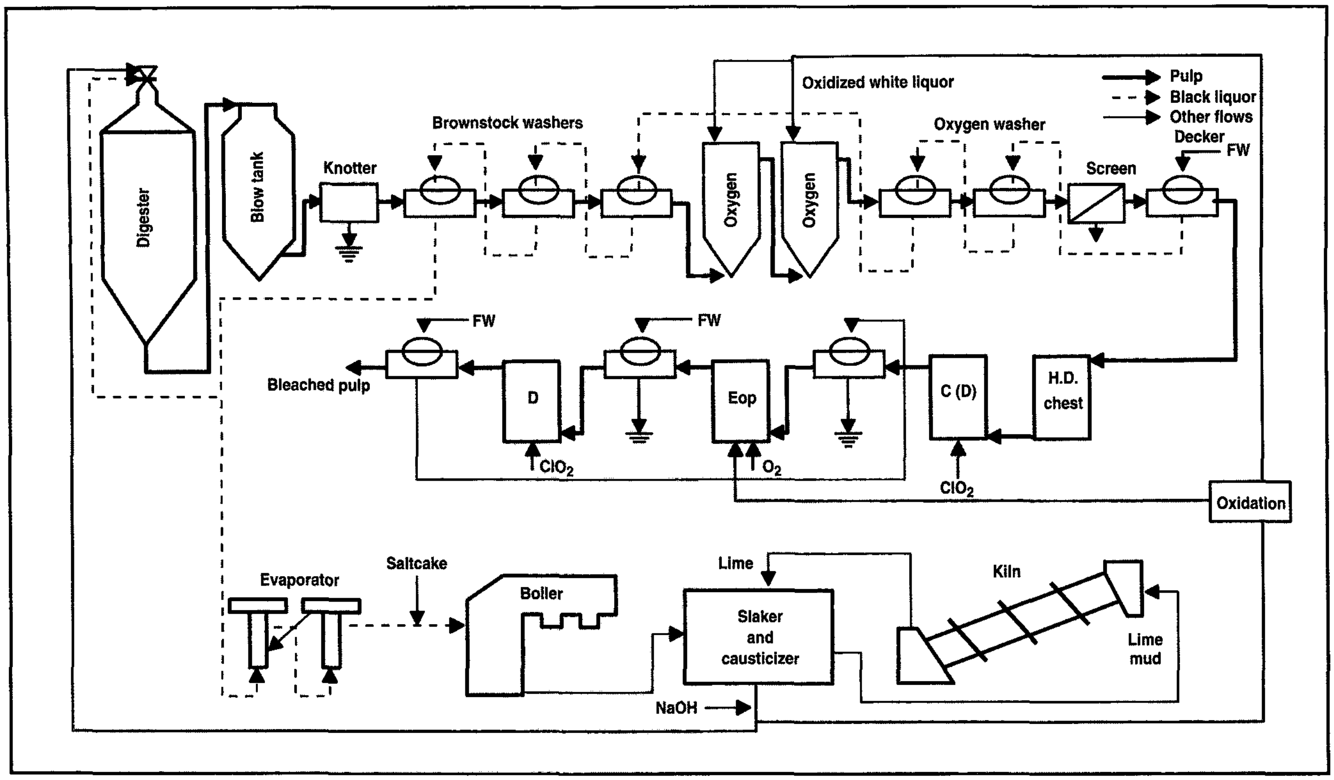
Steady-state simulation was used in this study in two ways. Initially the data collected in the laboratory on alkali, H-factor, yield, and rejects were used to run simulations of nine different cases, as listed in **Table VII.** From these nine cases, three were selected for further studies as the most promising both from an economic and a process standpoint. These choices were based primarily on the boiler load and the projected operating costs. The cases chosen are 30(O), 40(OO), and 50(OO), as indicated in Table VII.

For the three selected cases, additional laboratory data on bleaching response in ECF and TCF sequences and strength properties were collected, as described in the experimental section. Additional simulations for the three cases and a conventional base case were then run for the final economic evaluation.

The simulation studies used GEMS (General Energy and Material Balance System)*(2)*. A conventional flowsheet consisting of batch digesters, a three-stage brownstock washing system and screening system, a recovery system, and a C_DEoD bleaching system with 50% chlorine dioxide substitution was used for the initial runs. The oxygen stage (or stages) with two washers was inserted between the brownstock washers and screening, as required for the various cases. The bleached production was held constant in all cases, and the chip flow adjusted accordingly as yield varied.

The final simulation for the three selected cases included ECF and TCF bleaching sequences. Schematics of the complete fiber line and recovery for a two-stage oxygen system with ECF and TCF bleaching sequences are shown in **Figs. 7 and 8**, respectively. Kappa 30 without oxygen delignification was considered the base case for the simulations with ECF sequences, and kappa 30 with one-stage oxygen delignification was considered the base case for simulation with TCF bleaching. White liquor from recovery, oxidized to sulfate, is used for the alkali requirements of oxygen delignification and bleaching. The effluents from pulping and oxygen delignification are sent to recovery in all of the cases. The acidic and alkaline effluents of the ECF sequences are kept separate, and effluent from the chlorine dioxide stage is recycled for washing of pulp from the chlorination stage and finally discharged. The effluents from the TCF sequences are recycled to wash the previous-stage pulp, and ultimately are sent to the recovery system for recovery of chemicals and energy. The descriptions of the cases are given in **Table VIII.** Simulation re-

7. Two-stage oxygen ECF sequence



sults are listed in **Tables IX and X,** which include both the operating results, such as makeups, steam usage, and steam production, as well as the economics for the various cases.

ECF sequences

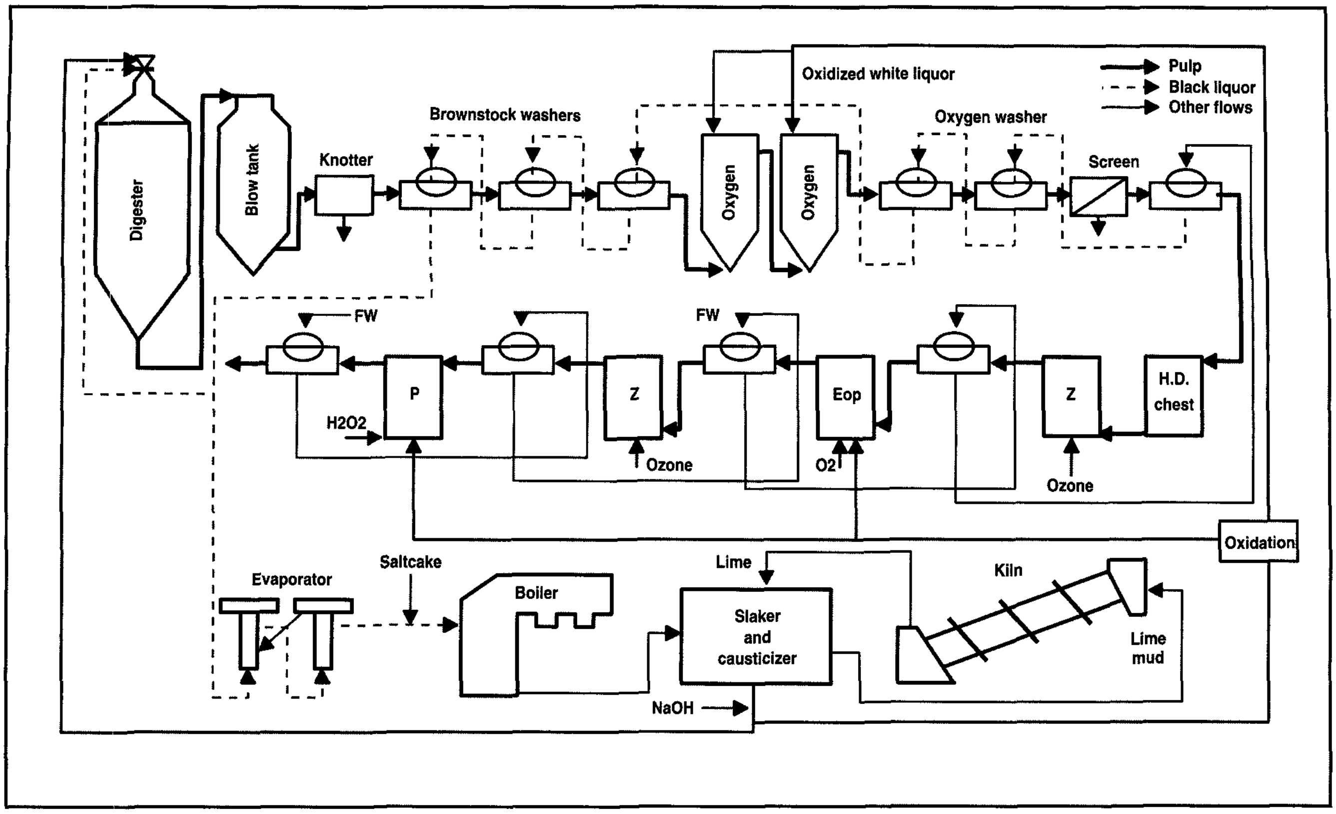
Impact on the boiler. Dissolved solids to the boiler increase by about 4% from the Base Case (30 ECF) to the case with single-stage oxygen delignification [30(O) ECF], changing from 4.87 MM lb/day for the Base Case to 5.04 MM lb/day for Case 30(O) ECF (Fig. 9). By pulping to 40 kappa followed by two-stage oxygen delignification, the boiler load is slightly lower than Case 30-ECF, due mainly to the lower chip flow required for the constant bleached production. As a result, it would be possible to implement a 40(OO)-ECF sequence in a mill without increasing the recovery load to the boiler. The load on the boiler further decreases from Case 40(OO)-ECF to Case 50(OO)-ECF by about 10%, from 4.67 MM lb/day to 4.19 MM lb/day. The recovery load is lowest for Case 50(OO)-ECF compared to all other cases. This lower recovery load may be used for incremental production by mills that are recovery-limited. Table IX also shows that the energy input in MM Btu/h follows the same trend as the solids loading in all cases. The decreases in energy generated in cases 50(OO)-ECF and 40(OO)-ECF relative to the Base Case (30-ECF) are due to both lower organics to the boiler from decreased chip input and lower heating value of the oxygen organics.

BOD and AOX. The AOX generated in the bleach plant is directly proportional to the kappa number of the pulp going to the bleach plant *(3)*. The kappa number to the bleach plant for Case 40(OO)-ECF is 13, compared to 15.5 for Case 30(O). Thus, BOD and AOX values for 40(OO)-ECF are less than the 30(O)-ECF, mainly due to the lower chip flow and the lower kappa number to the bleach plant for the 40(OO)-ECF case.

Economics. Cost per o.d. ton of ECF pulp decreases from the Base Case (US$ 197.10/o.d. ton) to Case 30(O)-ECF (US$ 185.30/o.d. ton), a savings of US$ 12/o.d. ton (Fig. 10). The cost per ton of pulp goes down further from Case 30(O)-ECF to 40(OO)-ECF and 50(OO)-ECF. The major factor contributing to the lower cost is the lower chip consumption at constant bleached pulp production due to higher yields in the double-stage oxygen cases, compared to the 30(O) Case. The cost per ton of pulp for Case 50(OO)-ECF is the lowest and is about US$ 13 less than the Base Case (30-ECF). Case 50(OO)-ECF is the most attractive sequence from a cost standpoint.

Although 50(OO)-ECF has the lowest cost, other factors must be considered when determining the most feasible option. For instance, the environmental impact for

8. Two-stage oxygen TCF sequence



40(OO)-ECF is less than 50(OO)-ECF, since the kappa number entering the bleach plant from 40(OO)-ECF is less than 50(OO)-ECF. This in turn leads to lower chlorine dioxide use for a lower AOX and less organic removal in bleaching for a lower BOD. At the same time, 40(OO)-ECF has an environmental impact less than or comparable to the "conventional" cases, 30-ECF and 30(O)-ECF. In terms of recovery boiler load, Case 40(OO)-ECF is also lower than 30(O)-ECF and similar to 30-ECF. In addition, the strength properties of 40(OO)-ECF are better than 50(OO)-ECF and slightly lower than 30(O)-ECF. Thus, Case 40(OO)-ECF is the best option for the ECF sequences.

In summary, Case 40(OO)-ECF could be implemented in either a conventional kraft or kraft/oxygen mill with little or no impact on the boiler and effluent treatment at an operating cost lower than the conventional cases. The better strength properties at only slightly higher cost make Case 40(OO)-ECF more attractive than Case 50(OO)-ECF.

VIII. Description of cases

Case	*Kappa brown pulp*	*No. of oxygen stages*	*Kappa bleach plant*	*Bleacing sequences*	*Case nomenclature*
Base case	30	...	30	DEopD	30 ECF
Case 1	30	1	15.5	DEopD	30(O) ECF
Case 2	40	2	13	DEopD	40(OO) ECF
Case 3	50	2	17	DEopD	50(OO) ECF
Case 4	30	1	15.5	ZEopZP	30(O) TCF
Case 5	40	2	13	ZEopZP	40(OO) TCF
Case 6	50	2	17	ZEopZP	50(OO) TCF

TCF sequences

Impact on boiler. The load on the boiler increases from Case 30-ECF to 30(O)-TCF, from 4.9 MM lb/day to 5.5 MM lb/day. As a result it would not be possible to implement TCF bleaching without increasing the recovery load significantly. On the other hand, dissolved solids to the boiler decrease from Case 30(O)-TCF to 40(OO)-TCF and 50(OO)-TCF from 5.5 MM lb/day to 5.1 and 4.6 MM lb/day. The load on the boiler is lower for Case 50(OO)-TCF (4.6 MM lb/day) as compared to the load

IX. Simulation results for ECF sequences

	Unit	30-ECF	30(O)-ECF	40(OO)-ECF	50(OO)-ECF
Fiber line					
Kappa brown pulp		30	30	40	50
Kappa to bleach plant		30	15.5	13	17
Chips	ODTC/day	2762	2756	2635	2522
Production					
Brown pulp	ODTBR/day	1196	1193	1221	1244
Post-oxygen brown pulp	ODTX/day	......	1155	1152	1159
Bleached pulp	ODT/day	1100	1100	1100	1100
Yield, %					
Pulping		43.3	43.3	46.3	49.3
Post-oxygen		......	41.9	43.7	45.9
Bleaching (overall)		39.8	39.9	41.8	43.6
White liquor					
Flow	g/m	951	955	820	694
Active alkali as Na_2O	%	19.8	19.8	17.8	15.8
Sulfidity	%	25	25	25	25
Digester steam	lb/ODT	4674	4613	4378	4159
Vapor generated	lb/ODT	3403	3396	3219	3057
Water used pulping	gal/min	2091	2091	2091	2091
Oxygen stage					
Oxidized white liquor flow	gal/min	0.0	46.1	111.1	112.7
Oxygen used	lb/ODT	0.0	57.4	106.9	130.7
Organic carryover	lb/ODTBR	19.9	3.8	5.0	6.1
Inorganic carryover	lb/ODTBR	8.3	4.2	7.0	7.5
Steam used (oxygen + bleaching)	lb/ODT	1230	1596	1608	1605
Oxygen used for white liquor oxidation	lb/ODT	0.0	16.3	39.3	39.8
Stage C(D)					
Substitution	%	100	100	100	100
Kappa factor	...	0.22	0.22	0.22	0.22
H_2O_2 used	lb/ODT	5.3	5.2	5.2	5.2
ClO_2 used	lb/ODT	80.3	48.5	44.4	51.9
Stage Eop					
Caustic charge	%	3.95	2.05	1.72	2.24
Oxygen used	lb/ODT	10.0	10.0	10.0	10.0
Oxidized white liquor flow	gal/min	70.9	36.2	30.2	39.9
Oxygen used for white liquor oxidation	lb/ODT	25.1	12.8	10.7	14.1
Stage D					
ClO_2 charge	%	1.00	1.00	1.00	1.00
Water used (bleaching)	gal/min	2794	2794	2794	2794
BOD bleach plant	lb/h	8051	4355	4214	4647
AOX	lb/ODT	4.22	2.55	2.33	2.73
		Recovery			
Evaporator					
Flow to evaporator	gal/min	1899	2032	1933	1766
Solids to evaporator	%	18.1	17.6	17.2	16.8
Dissolved solids to evaporator	lb/ODT	4108	4290	3976	3559
Steam used (evaporated)	lb/ODT	3028	3285	3169	2925
Steam used (concentrated)	lb/ODT	1053	1100	1019	912
Boiler					
Solid fired boiler	%	66.7	66.5	66.5	66.5
Dissolved solids to boiler	MM lb/day	4.87	5.04	4.67	4.19
Inorganic at boiler	MM lb/day	1.66	1.74	1.64	1.44
Organic at boiler	MM lb/day	3.21	3.30	3.03	2.75
Energy available	MM Btu/h	789	804	729	665

Slaker					
Reburned lime	lb/ODT	755	800	738	634
Fresh lime	lb/ODT	22.2	23.6	23.7	22.8
Make-up lime	tons/day	0.012	0.013	0.013	0.013
White liquor make-up					
NaOH (make-up)	lb/ODT	126.9	80.3	74.8	84.2
Na_2SO_4	lb/ODT	68.8	41.0	37.1	43.1
Elemental sulfur	lb/ODT	0.0	0.0	0.0	0.0
Kiln					
Throughput	ODT/day	314	333	308	264
Fuel	tons/day	73	78	72	62
Water usage recovery	gal/min	1025	1043	967	850
Steam used in recovery	lb/ODT	95	85	82	82

Cost analysis

	Cost, US$	*30-ECF*	*30(O)-ECF*	*40(OO)-ECF*	*50(OO)-ECF*
Chips/kg	0.062	153.68	155.34	148.48	142.15
H_2O_2/lb	0.573	3.04	2.98	2.97	3.00
ClO_2/lb	0.300	24.10	14.54	13.31	15.58
NaOH/lb	0.141	17.89	11.32	10.55	11.88
Na_2SO_4/lb	0.050	3.44	2.05	1.85	2.16
Elemental sulfur/lb	0.070	0.00	0.00	0.00	0.00
Fresh lime/lb	0.032	0.71	0.75	0.76	0.73
Steam used/kg	0.006	27.49	29.13	27.97	26.41
Kiln fuel/barrel	20.00	8.83	9.46	8.75	7.49
Water/1000 gal	0.072	0.56	0.56	0.55	0.54
BOD/kW·h	0.025	0.90	0.49	0.47	0.52
Oxygen/lb	0.040	1.40	3.86	6.68	7.78
$MgSO_4$/lb	0.223	0.00	2.66	5.44	5.55
Total	...	244.03	233.15	227.78	223.78
Energy available/ODT	...	46.97	47.82	43.38	39.59
Net cost	...	197.1	185.3	184.4	184.2

ODT = oven-dry ton bleached pulp. ODTBR = oven-dry ton brown pulp. ODTC = oven-dry ton of chips. ODTX = oven-dry ton oxygen pulp.

for Base Case 30-ECF (4.9 MM lb/day). Thus, 50 (O)(O)TCF can be retrofitted into a conventional kraft mill without increasing the recovery load. If the base case for the mill with regard to recovery boiler load is 30(O)-ECF at 5.0 MM lb/day, then both TCF sequences 40(OO)-TCF, at 5.1 MM lb/day, and 50(OO)-TCF, at 4.6 MM lb/day, may be viable options.

Chemical makeup. In the simulation of TCF sequences, if fresh alkali is used in bleaching and all of the effluent is recycled to the recovery system, sodium levels in the system will exceed makeup requirements. The possible options to maintain the sodium balance in the system are to purge in the recovery system, to split some of the ozone-effluents to sewer, or to use oxidized white liquor for bleaching *(4)*. Oxidized white liquor (conversion of sulfide to sulfate) for bleaching was used in all of the simulation cases, as stated earlier *(5)*.

Economics. The cost per ton of pulp for Case 30(O)-TCF (US$ 223.90), is higher than Case 30(O)-ECF (US$ 185.30). This increase in cost is due to the higher cost of ozone and higher yield losses. Cost per ton of pulp decreases from Case 30(O)-TCF (US$ 223.90) to Case 50(OO)-TCF(US$ 219.50), due in large part to the reduction in chip consumption as discussed in the ECF cases.

Since the strength properties of all the TCF pulps with oxygen delignification are comparable, and there is no effluent in the TCF sequence, the implementation of one of these sequences depends primarily on the recovery boiler load. If the mill is a conventional kraft system (i.e., Case 30-ECF), the 50(OO)-TCF is the only option that will give

X. Simulation results for TCF sequences

	Unit	*30(O)-ECF*	*40(OO)-ECF*	*50(OO)-ECF*
Fiber line				
Kappa brown pulp	...	30	40	50
Kappa to bleach plant	...	15.5	13	17
Chips	ODTC/day	2853	2740	2592
Production				
Brown pulp	ODTBR/day	1235	1269	1279
Post-oxygen brown pulp	ODTX/day	1196	1198	1191
Bleached pulp	ODT/day	1100	1100	1100
Yield, %				
Pulping	...	43.3	46.3	49.3
Post-oxygen	...	41.9	43.7	45.9
Bleaching (overall)	...	38.6	40.1	42.4
White liquor				
Flow	g/m	991	854	715
Active alkali as Na_2O	%	19.8	17.8	15.8
Sulfidity	%	25	25	25
Digester steam	lb/ODT	4774	4550	4273
Steam generated	lb/ODT	3511	3343	3137
Water used pulping	gal/min	0	0	0
Oxygen stage				
Oxidized white liquor flow	gal/min	47.9	115.8	116.3
Oxygen used	lb/ODT	57.4	106.9	130.7
Organic carryover	lb/ODTBR	215.1	220.4	203.9
Inorganic carryover	lb/ODTBR	197.1	199.8	196.9
Steam used (oxygen + bleaching)	lb/ODT	1254	1265	1262
Oxygen used for white liquor oxidation	lb/ODT	16.9	40.9	41.1
Bleaching				
Ozone charge Z1 ST	%	0.75	0.75	0.75
Ozone charge Z2 ST	%	0.52	0.52	0.52
H_2O_2 used	lb/ODT	45.7	45.6	45.6
Ozone used	lb/ODT	27.0	27.0	26.9
H_2SO_4 used	lb/ODT	21.6	21.6	21.5
Oxidized white liquor flow	gal/min	77.4	77.4	77.1
Caustic charge Eop	%	3.0	3.0	3.0
Caustic charge P ST	%	1.3	1.3	1.3
Oxygen used in Eop	lb/ODT	10.0	10.0	10.0
DTPA used	lb/ODT	4.04	4.03	4.03
Purge Z effluent	%	0	0	0
Water used (bleaching)	gal/min	2752	2752	2752
BOD bleach plant	lb/h	0	0	0
AOX	lb/ODT	0	0	0
Oxygen used for white liquor oxidation	lb/ODT	27.4	27.4	27.3
		Recovery		
Evaporator				
Flow to evaporator	gal/min	2178	2078	1898
Solids to evaporator	%	18.1	17.8	17.3
Dissolved solids to evaporator	lb/ODT	4721	4422	3933
Steam used (evaporated)	lb/ODT	3469	3344	3100
Steam used (concentrated)	lb/ODT	1211	1134	1008
Boiler				
Solid fired boiler	%	66.3	66.3	66.2
Dissolved solids to boiler	MM lb/day	5.5	5.1	4.6
Inorganic at boiler	MM lb/day	1.9	1.8	1.6
Organic at boiler	MM lb/day	3.6	3.3	3.0
Energy available	MM Btu/h	858	785	709

Slaker				
Reburned lime	lb/ODT	871	812	697
Fresh lime	lb/ODT	24.6	24.8	24.0
Make-up lime	tons/day	0.014	0.014	0.013
White liquor make-up				
NaOH (make-up)	lb/ODT	70.9	71.0	69.0
Na_2SO_4	lb/ODT	1.9	1.6	1.9
Elemental sulfur	lb/ODT	0.0	0.0	0.0
Kiln				
Throughput	ODT/day	364	339	291
Fuel	tons/day	85	79	68
Water usage recovery	gal/min	1123	1054	915
Steam used in recovery	lb/ODT	81	80	77

Cost analysis

	Cost, US$	*30(O)-TCF*	*40(OO)-TCF*	*50(OO)-TCF*
Chips/kg	0.062	160.97	154.43	146.11
H_2O_2/lb	0.573	26.18	26.15	26.12
Ozone/lb	1.000	27.02	27.03	26.91
NaOH/lb	0.141	10.00	10.01	9.73
Na_2SO_4/lb	0.050	0.10	0.08	0.10
Elemental sulfur/lb	0.070	0.00	0.00	0.00
Fresh lime/lb	0.032	0.79	0.79	0.77
Steam used/kg	0.006	29.42	28.29	26.51
Kiln fuel/barrel	20.00	10.28	9.62	8.25
Water/1000 gal	0.072	0.37	0.36	0.35
BOD/kW·h	0.025	0.00	0.00	0.00
Oxygen/lb	0.040	4.47	7.41	8.36
$MgSO_4$/lb	0.223	2.75	5.66	5.70
H_2SO_4/lb	0.032	0.69	0.69	0.69
DTPA/lb	0.510	2.06	2.06	2.05
Total	...	274.89	272.57	261.65
Energy available/ODT	...	51.03	46.70	42.17
Net cost	...	223.9	225.9	219.5

ODT = oven-dry ton bleached pulp. ODTBR = oven-dry ton brown pulp. ODTC = oven-dry ton of chips. ODTX = oven-dry ton oxygen pulp.

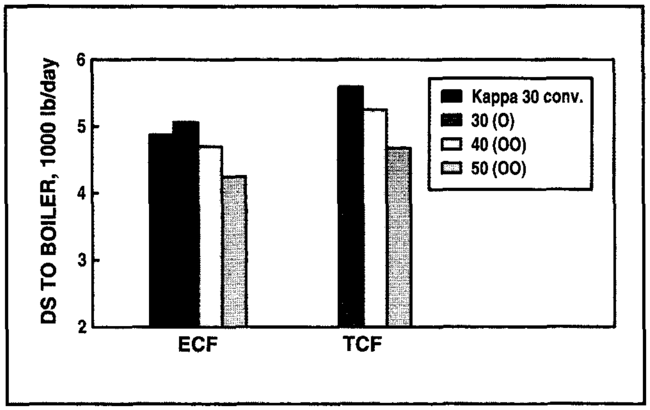
a similar or lower recovery load. If, on the other hand, the recovery load is to remain the same as 30(O)-ECF, both 40(OO)-TCF and 50(OO)-TCF are viable options.

In summary, the technology of pulping to a high kappa number followed by two-stage oxygen delignification will allow the recycling of the bleach plant effluents to the recovery boiler without increasing its load as compared to extended kraft delignification or conventional oxygen delignification. For Case 50(OO) with TCF bleaching, the load on recovery is less than Base Case 30-ECF. This means a recovery-limited kraft mill can use two-stage oxygen delignification with complete recycle of bleach plant effluents (TCF sequence) without increasing the load on the recovery system.

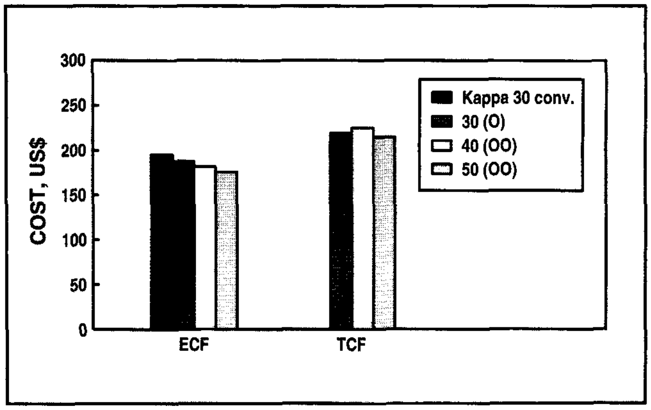
Conclusions

1. Conditions to produce a kappa number 30 pulp are 20% active alkali and 1100 H-factor. Conditions to pulp to kappa numbers of 40 and 50 are active alkali of 17.8% and 15.8%, respectively, and H-factor of 1100.
2. Pulping to higher kappa number leads to higher rejects. Oxygen delignification reduces the rejects from pulping by 77%. Two-stage oxygen delignification further reduces the rejects by 96% of the original pulp rejects in the case of a 40-kappa number pulp.
3. Percentage delignification observed for 30-kappa number pulp with one-stage oxygen delignification at 3% alkali is 55.8%;

9. Boiler load



10. Cost per ton



delignification observed for 40- and 50-kappa number pulps with two-stage oxygen delignification are 70.1% and 69.5%, respectively, with 3% alkali charge in each stage.

4. Brightness for two-stage oxygen delignification cases without interstage washing is higher than that with washing between the two oxygen stages. The yields for both interstage washing and no interstage washing are comparable.

5. Using a bleaching sequence of DEopD, the brightnesses achieved for 30-ECF, 30(O)-ECF, 40(OO)-ECF and 50(OO)-ECF pulps are 83.5, 85, 86, and 84 ISO, respectively.

6. Brightnesses achieved for cases 30-TCF, 30(O)-TCF, 40(OO)-TCF, and 50(OO)-TCF with a bleaching sequence of ZEopZP are: 70, 86, 87, and 87 ISO, respectively. Yield losses are higher for TCF sequences than ECF sequences.

7. The tear and tensile for 40(OO)-ECF pulp is less than the conventional 30-kappa number pulp by 3.6% and 6.7%, respectively, at a freeness of 390 CSF. Strength properties of TCF pulps are significantly lower than those of ECF pulps. Strength properties of all the TCF oxygen pulps are comparable.

8. Although 50(OO)-ECF has the lowest cost, other factors must be considered when determining the most feasible option. For instance, the environmental impact for 40(OO)-ECF is less than 50(OO)-ECF. At the same time, 40(OO)-ECF has an environmental impact less than or comparable to the conventional cases—30-ECF and 30(O)-ECF. In terms of the recovery boiler load, Case 40(OO)-ECF is also lower than 30(O)-ECF, and similar to 30-ECF. In addition, the strength properties of 40(OO)-ECF are better than 50(OO)-ECF and slightly lower than 30(O)-ECF. Thus, 40(OO)-ECF is the best option for ECF sequences.

9. Since the strength properties of all the TCF pulps with oxygen delignification are comparable, if the base recovery load is Case 30-ECF, then 50(OO)-TCF is the only option with a similar or lower recovery load. If the base recovery load is 30(O)-ECF, both 40(OO)-TCF and 50(OO)-TCF are viable options. TJ

Literature cited

1. Markham, L. D., Courchene, E., Elton, E. F., *et al.*, *TAPPI 1981 Pulping Conference Proceedings, and* TAPPI PRESS, Atlanta, p. 165.
2. Edwards, L. L. and Haynes, J., *Documentation for General Energy and Material Balance System*, Idaho Research Foundation, Moscow, ID, 1989.
3. Kringstad, K. P. and McKague, A. B., *TAPPI 1988 International Pulp Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta, p. 69.
4. Shackford, L. D. and Minami, S., Impact of Ozone Bleaching and Total Chlorine Free Bleaching on Mill Sodium/Sulfur Balance, Non-Chlorine Bleaching Conference, Hilton Head, SC, 1993.
5. Ayala, V., Magnotta, V., O'Czerny, A., *et al.*, *TAPPI 1990 Oxygen Delignification Symposium Notes*, TAPPI PRESS, Atlanta, p. 153.

Received for review Aug. 10, 1993.

Accepted May 29, 1994.

Presented at the TAPPI 1993 Pulping Conference.