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Title: The Bleaching Response of Kraft Pulps from Fresh and Aged Commercial Douglas-fir Chips

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The effects of commercial Douglas-fir aged chips on the properties of unbleached pulp were investigated in bomb cooks using the pulping variables of time, temperature, chemical charge, and sulfidity. It was found that at the same kraft pulping conditions the pulps from aged chips had lower yields, lower Kappa numbers, but higher unbleached brightness than the pulps from fresh chips; in the waste liquor, the pH and the residual alkali from aged chip pulping are both lower than those in waste liquor from fresh chip pulping. Using chemical charge as the only controlling variable, three sets of kraft pulps (pulp from aged chips, from fresh chips, and from a 50:50 blend of aged and fresh chips) were made with varying Kappa numbers in a circulating digester.

At the same Kappa number, the unbleached brightness of aged chip pulp (AP) is slightly lower than that of fresh chip pulp (FP). When the pulps of identical Kappa numbers were bleached, small differences in NaOCl bleachability were observed between AP and FP. However, in commercial five-stage (CEDED) bleaching, the bleaching response of AP is superior to the response of FP, in spite of the inferiority of the former

in unbleached pulp brightness. A strong relationship was found between NaOCl bleached brightness and five-stage bleached brightness.

A permanganate number was determined at the end of the CE_1 bleaching stages (CE_1-K number). At the same Kappa number of unbleached pulp, the CE_1-K number of AP was lower than that of FP, which implied that the delignification rate in AP was more rapid than in FP.

The viscosity of AP is substantially lower than that of FP, which confirmed the degradation of aged chips.

The Bleaching Response of Kraft Pulps from Fresh and Aged Commercial Douglas-fir Chips

by

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THE BLEACHING RESPONSE OF KRAFT PULPS FROM FRESH AND AGED COMMERCIAL DOUGLAS-FIR PULPS

INTRODUCTION

In a period of rising wood costs, the effect of aged wood on the economy and operation of a kraft mill is of increasing importance. The aged wood can be derived from two primary sources: (a) rotted wood being procured as a result of more intensive forest management practices, i.e., logs that are being brought out of the woods that previously were left behind to rot or be burned as slash; and (b) chips that are "aged" by being stored in a chip pile for varying lengths of time under varying conditions.

This study is concerned only with the aged wood from chip piles. During outdoor chip storage, a combination of physiological, microbial, and chemical reactions cause heating of the pile, which can do severe damage to the wood. Compared to fresh wood, aged wood is characterized by darker color, lower density, higher rot content, higher acidity, and higher alkali solubility. These factors will result in a pulp from aged wood with lower yield and darker color than a pulp from fresh wood at the same Kappa number. In more extreme cases of wood degradation, the resulting pulps may be physically weaker than normal.

Lignin, acting as a binder to hold the fibers together, is one of the major components in wood. During chemical pulping (the first stage of delignification) enough lignin should be removed so that the fibers can be separated from each other. Due to its absorption of light, lignin is known to be responsible for the color of unbleached pulp. The more lignin remaining in the pulp, the darker the color.

The Kappa number test, which is widely used in kraft mills, is the measure of lignin content in a pulp. The higher Kappa number implies more lignin content, hence it is used as a criterion for bleaching (the second stage of delignification): the higher the Kappa number of the unbleached pulp, the greater the amount of bleaching chemicals that will be needed to attain any given brightness level of the bleached pulp.

Lacking knowledge of the bleaching response of pulp from aged wood, it is not known if an aged wood pulp can be bleached to the same brightness level as a fresh wood pulp, assuming that both pulps have the same Kappa number and are treated with equivalent bleaching sequences. In this project we seek the answers for these questions.

The pulping materials (aged wood and fresh wood) used in this research were so-called commercial Douglas-fir chips. These chips contain a minimum of 80% Douglas-fir and a maximum of 20% other softwood species. This is a commercial trade term generally used in the Pacific Northwest pulping industry.

The objectives of this research are:

1. To determine the bleachability of kraft pulps made from fresh and from aged commercial Douglas-fir chips as a function of the Kappa number.

2. To determine if a single stage bleachability test can be used to predict the bleaching response of these pulps subjected to full scale multi-stage bleaching sequences.

3. To examine the yields and viscosities of the pulps made from fresh and aged chips and relate to chip quality.

LITERATURE REVIEW

Aging of Wood

Aging of wood is a complex and diverse process, complicated by the many varieties of microorganisms that can attack and destroy wood, plus the multitude of chemical reactions that are possible. Aging can occur in a living tree (rot or decay) or in a chip pile. Tree rot may be divided broadly into brown-rot or white-rot types. Brown-rot decay results primarily in degradation of the carbohydrate portion of wood whereas white-rot attacks both carbohydrates and lignin (1). Consequently, brown-rotted wood generally has a higher lignin content than sound wood or white-rotted wood. These degraded components in wood are more soluble in alkali than normal, so that an increase in one percent alkali solubility could indicate the degree of decay present (10). However, the aging which occurs in a chip pile is more complicated because it is the result of both microbial action and heating. Therefore, aged chips may include rotted (brown-rot or white-rot or both) chips from trees and normal degraded chips (no rot symptoms). The aging may cause irreversible damage to the wood chips; approximately 1 to 1.5 percent wood losses by weight per month have been reported (2, 3). Other effects of degradation have been observed (4, 5, 6, 7): relative to a fresh wood, aged wood had a darker color, greater acidity, and lower density.

Reported Effects of Aged Wood on Kraft Pulping

With respect to kraft pulping, both rot types must result in some pulp yield losses calculated on original wood volume (1); also, the pulp yield calculated from original wood weight is lower for brown-rotted wood, but is not markedly affected with white-rotted wood. Kawase and Igarashi (16) reported that there was little difference in unbleached pulp brightness between sound wood pulp and white-rotted wood pulp, while brown-rotted wood pulp had a lower unbleached brightness. Cowling (1) found that brown-rot severely reduced the DP (degree of polymerization) of cellulose which will result in weaker pulp fibers, and hence reduced paper strength properties, but, in contrast with brown-rot, white-rot results in only a small loss in cellulose DP. Consequently, only minor strength losses would be expected with pulp from white-rotted wood. A study of disk chipping and screening of decayed wood was reported by various researchers (16, 19), and it is generally agreed that less accepts and more pin chips and fines were produced from decayed than from sound wood. Hunt (19) recommended that pin chips and fines be removed from the accepts by screening prior to pulping so that a more rigorous control of pulping conditions could be maintained. In studying kraft pulping behavior of decayed pulp wood, a negative linear relationship bewteen one percent caustic solubility and pulp yield was found by Hatton and Hunt (18).

The effects of aged chips on the properties of unbleached kraft pulp were studied by Bublitz (4, 5, 6, 7), who found that, at the same Kappa number, the pulps from aged chips had darker color than the pulps from fresh chips. Aged chips generally consume more pulping chemical and produce lower pulp yields than the fresh chips. Regarding the pulp strength, Bublitz suggested that advanced stages of wood degradation can yield pulps with lower physical strengths than pulps from fresh chips. This phenomenon is more variable than the others, however, and to some extent is a function of the type of degradation.

Bleaching Response of Pulps from Aged Wood

No quantitative information on the bleaching response of pulps produced from rotten wood could be found in the literature. However, some incomplete studies (17) suggested that the pulps from the white-pocket Douglas-fir appeared to bleach easier than those from the sound wood. Kawase and Igarashi (16) claimed that there was little difference between sound wood pulp and cellulose-rich decayed (white-rotted) wood pulp in bleaching response, while the bleachability of lignin-rich decayed (brown-rotted) wood pulp was inferior. The rotted wood used as the pulping materials in the above studies were tree-rot types.

In searching the literature the writer failed to find anything with regard to the bleaching response of pulps from aged wood from chip piles.

Determination of Lignin in Unbleached Pulps

The Kappa number and K number tests are used to measure the lignin content of the unbleached pulp and thereby its bleachability. The Kappa number test may be used for all types and grades of chemical and semichemical, unbleached and semibleached wood pulps obtained with a yield of under 70 percent. However, the K number test provides for pulps having a lignin content below six percent.

TAPPI Standard T 236 m-60 (21) states: "The Kappa number gives essentially a straight line relationship with Klason lignin. The percentage of Klason lignin approximately equals (Kappa number) x 0.15."

Consequently, more chemicals are required to bleach a pulp with a higher Kappa number. Hinrichs (20) proposed that a 4.0 CE-K number (after chlorination and extraction) was necessary for efficient bleaching (brightness 90) with the CEDED sequence (0.9 percent total ClO_2 charge).

Pulp Brightness and Bleaching

The brightness of a pulp is the measure of the percent reflectance of paper (a sheet pad formed from pulp fibers) at a narrow band of light with a dominant wavelength of 457 nm (blue light) (21), relative to the reflectance of MgO, taken at 100 percent. Therefore, the mechanism of bleaching is to either change or remove the light-absorbing substances in the pulps.

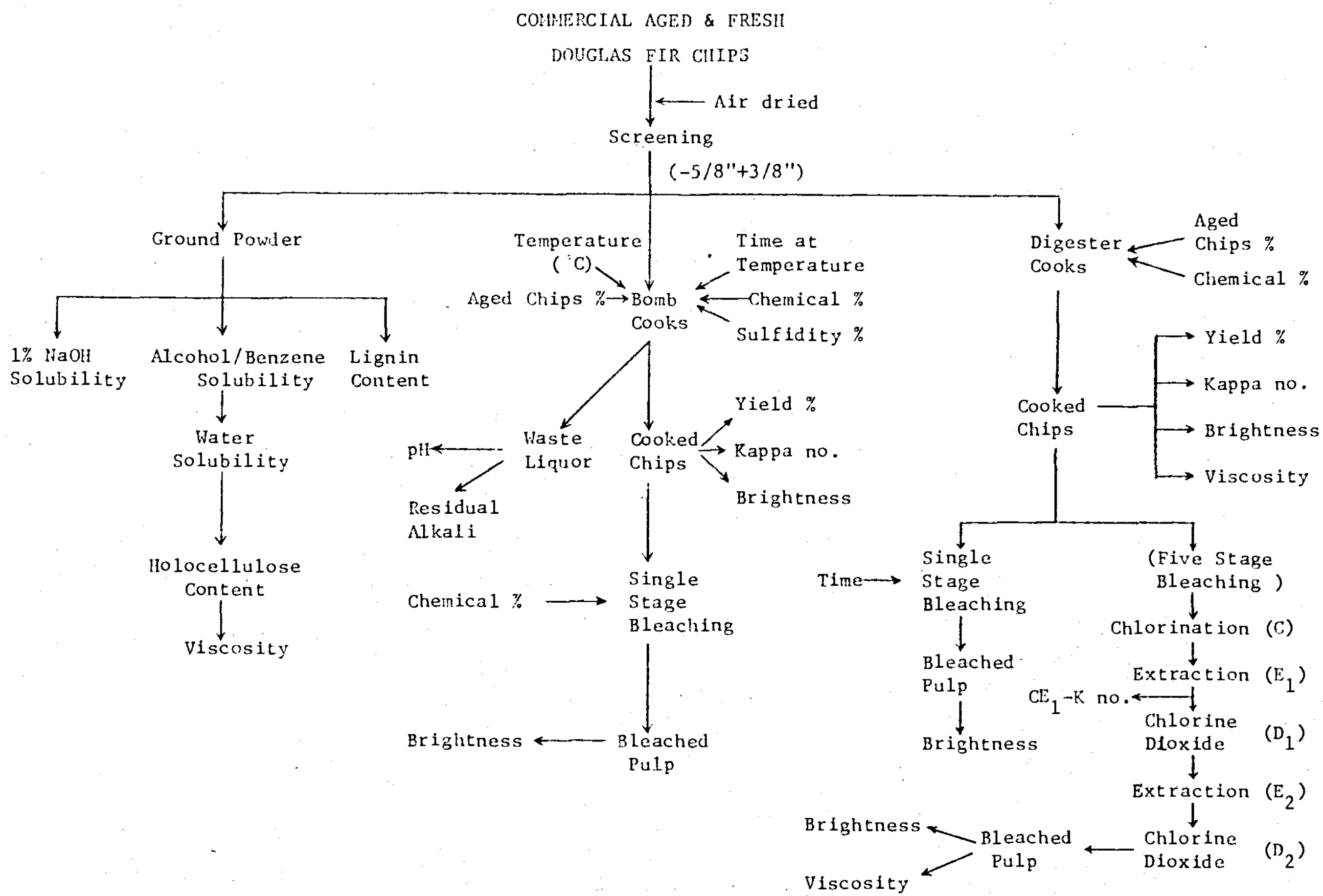
Rapson (15) states:

> The main light-absorbing substances in wood pulp are derived from the lignin and resin components of the original wood. Therefore, to make pulp white, these substances must either be chemically changed in the solid state to diminish their light-absorbing characteristics, or be oxidized, reduced, or hydrolyzed to make them soluble in aqueous solutions in order to remove them from the pulp....Carbonyl groups in any organic compound may be responsible for much of the color in pulp, as well as for the yellowing which occurs on aging.

Usually, lignin-bleaching methods are used for high yield mechanical pulps. For most cases, they are just a single-stage or at most two-stage bleaching. The increments of brightness are not very much, however, they are sufficient for their purposes. When a higher brightness is desired it is necessary to apply lignin-removing methods, which are of interest for chemical and some grade of semichemical pulps. The lignin removal is usually done in several stages, called multi-stage bleaching. Usually, chlorine is used in the first stage since chlorine preferentially reacts with lignin and makes it soluble in water and alkali (15). A mild alkaline extraction following the initial chlorination reduces the requirement of subsequent bleaching chemicals and allows a higher brightness to be achieved. Then certain other oxidizing chemicals (ClO_2, NaClO, etc.) or reducing chemicals (e.g. $NaBH_4$) are used sequentially in an optimum bleaching sequence to reach a desired brightness level. Hinrichs (20) reported that kraft pulp can be bleached to 90 brightness and with superior viscosity, strength, and brightness reversion characteristics by CEDED bleaching.

EXPERIMENTAL

MATERIAL FLOW SHEET



Sample Collection and Preparation

Four barrels of commercial Douglas-fir [Pseudotsuga menziesii (Mirb.) Franco] chips were obtained from Roseburg Lumber Company near Coos Bay, Oregon, two of which contained aged chips collected from a chip pile built three years ago. The sampling spot was one foot below the top of that pile. The other two barrels of fresh chips were collected from the perimeter of a pile that had been built two months previously.

Both the aged and fresh chips were air dried for several days at the Forest Research Laboratory. A fan was used to increase the air circulation and speed the chip drying. This also cut down the microbial action and decreased further degradation of the chips.

Random samples of aged chips and fresh chips were screened separately using the Williams chip classifier, and the chips were classified into the following fractions: +1 1/8", -1 1/8" +7/8", -7/8" +5/8", -5/8" +3/8", -3/8" +3/16", -3/16" +1/16", and -1/16". In this study only the fraction -5/8" +3/8" (pass 5/8" screen, retained on 3/8" screen) was utilized for pulping. Then the chips were put into polyethylene bags and stored at room temperature to allow the moisture content to come to equilibrium.

Before making any cook, the obviously defective material such as knots, bark and dirt were removed by hand. A small amount of rotted chips was also found in the fresh chips, but it was assumed to be undesirable contamination and was also removed. The rotted chips found in the aged chips were not removed, however.

Wood Analysis

Approximately 200 grams each of aged and fresh chips were ground separately in a Wiley mill and screened through a 60-mesh screen as suggested by TAPPI Standard T 011 os-74).

The following standard tests were used in determining wood quality:

Subjects	TAPPI Standard
One percent caustic soda solubility	T 4m-59
Alcohol-benzene solubility	T 5 os-73
Hot water solubility	T 207 os-75
Holocellulose in wood	T 9m-54
Lignin in wood	T 222 os-74
Viscosity	T 230 su-66
pH of wood*	

*Ten grams (o.d. weight) of wood powder was dispersed in 100 ml of distilled water. After 24 hours the pH values of the solutions were determined with a digital pH meter (Orion 601A).

Bomb Cooks

A series of bomb cooks was made to investigate the effects of the variables of time, temperature, chemical charge, sulfidity and percentage of aged chips on the following response variables:

Pulp yield	Single stage bleachability
Kappa number	Residual alkali of waste liquor
Unbleached brightness	pH value in waste liquor

The levels of the variables are shown in Table 1, and the plan for the individual cooks is listed in Appendix 1.

Table 1. Kraft Pulping Variables and Levels for Bomb Cooks.

Variables	Code Value (Level) 1	2	3	4	5
Time at temperature (min.)	80	100	120	140	160
Maximum temperature (°C)	160	165	170	175	180
Chemical charge, active alkali (%)[a]	10	15	20	25	30
Sulfidity (%)[b]	10	15	20	25	30
Chip ratio (%)[c]	0	25	50	75	100

Liquor to wood ratio[d]	7:1
Digester type	Bomb cook
Heat system	Electric
Time to temperature	45 min.
Capacity	50 grams of o.d. wood

5x - variables N = 32 treatment combinations

1/2 replicate of 2^5 factorial + star design + 6 points in the center = 32

[a]Percentage of chemical charge (sum of NaOH + Na_2S both expressed as Na_2O).

[b]Sulfidity = $\frac{Na_2S}{NaOH + Na_2S}$ x 100 (all chemicals as Na_2O).

[c]0% of aged chips = 100% of fresh chips.

[d]Liquor to wood ratio: total weight of liquor (includes water in wet wood)/total weight of o.d. wood.

The variables were incorporated into a factorial experiment as described by Cochran and Cox (8). The plan does not include cooks at all possible levels of the factorial design. This would involve a total of 5^5 = 3,125 cooks, but with this design 32 cooks were involved.

The active alkali and sulfidity of the pulping liquors were measured by TAPPI Standard T 624 os-68, and the cooks were made according to the schedule.

After each cook the bomb was quickly cooled by quenching in cold water. As soon as the bomb was opened a sample of waste liquor was rapidly tested for pH and residual alkali in order to avoid further oxidation by air.

The cooked chips were disintegrated into pulp in a blender. The pulps then were filtered and washed in a Buchner funnel by water under the aid of suction. Thereafter, the washed pulps were dried in an oven (105 ± 3°C) for yield, Kappa number and unbleached brightness determinations.

Circulating-Digester Cooks

The variable, chemical charge, was found to be the most significant in controlling pulp yields, Kappa numbers, etc. Therefore, it was selected to be the only control variable in circulating-digester pulping in order to get three sets of four bleachable pulps (100-0%, 50-50%, and 0-100% ratio of fresh-aged chips) with Kappa numbers ranging from 20 to 40. The pulping plan for circulating-digester cooks is shown in Table 2.

Table 2. Plan of 12 Circulating-Digester Cooks

Ratio Fresh:Aged Chips	Active Alkali, % (as Na_2O)			
	20.0	22.5	25.0	30.0
100 - 0	1	4	7	10
50 - 50	2	5	8	11
0 - 100	3	6	9	12

Time to temperature = 45 min.

Time at temperature = 120 min.

Temperature = 170°C

Sulfidity = 20%

Liquor:Wood ratio = 7.5:1

Capacity = 900 gms of o.d. chips

The digester was heated with electric heaters which were regulated by a Honeywell Electronic Cam Controller.

At the end of each cook the chips were taken out of the digester and put into a polyethylene bag to allow the chips to cool and stabilize the moisture content. After the total wet weight of cooked chips was obtained, three 25 gm portions of cooked chips were taken for consistency determination using the same treatment as for bomb-cooked chips. The percentage of total yield (unscreened yield) was calculated by multiplying the total wet weight of cooked chips by the average consistency and divided by the moisture-free weight of the original chips.

The rest of the cooked chips were disintegrated into pulp using a laboratory disintegrator and screened in a Valley flat screener with an .008" cut plate. The screened yield was determined by subtracting the percentage of screened rejects from the total yield (all the calculations were based on the o.d. weight of original wood). Kappa numbers and unbleached brightnesses were determined on the screened pulps.

Waste Liquor Analysis

Samples of bomb cook waste liquors were tested for their pH value with a digital pH meter (Orion 601A).

For the residual alkali determination, 5 gm of waste liquor were titrated by standardized HCl to the end point of pH = 7.0.

Calculation for the amount of residual alkali:

$$\frac{(\text{Normality of HCl}) \times (\text{Volume of HCl}) \times (0.031)}{5} \times 1000$$

$= \text{gm } Na_2O/\text{kg liquor}$.

Pulp Testing

The Kappa numbers and 40 ml CE_1-K numbers were determined by TAPPI Standards T 236 m-60 and T 214 su-71, respectively. Brightnesses of the unbleached and bleached pulps were measured with filter no. 8 of the Elrepho colorimeter (TAPPI Standard T 525 su-72).

Single Stage Bleaching

In order to determine the bleachability of a pulp, a rapid method was developed from TAPPI Useful Method 206[1]. Eight grams of moisture-free basis pulp was suggested for the test. Calculated amounts of NaOCl[2] were added to a 2.7% consistency pulp slurry at 55°C. A pad was made in the British Handsheet Mold after the bleach chemical was consumed completely by the pulp. This could be observed by adding one or two drops of starch-KI indicator until the blue color would persist very faintly. The pads were dried at a temperature of 73°F and at a relative humidity of 50%.

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[1]TAPPI Useful Methods offers procedures claimed by their users to be satisfactory, but are not TAPPI Standard nor Suggested Methods. This method was prepared by R. H. Wiles, and is published for use by TAPPI members.

[2](a) 35% concentration of $Ca(OCl)_2$ was suggested by this method.

(b) 6% charge (based on o.d. pulp) was suggested, but due to the insufficient pulp yield of bomb cook only two runs of bleaching tests were allowed. Charges of 4% and 8% were selected for bomb-cook pulp; however, 6% charge was used in circulating-digester pulp.

(c) The strength of NaOCl was determined by TAPPI Standard T 611 m-47. Chemical reaction:

$$NaOCl + 2KI \rightarrow I_2 + NaCl + K_2O$$

$$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ KI$$

(Continued)

The above testing method was designed to be a rapid method, but some of the digester pulps with Kappa numbers less than 20 took two to four hours to consume all of the bleach chemical. Therefore, this method was modified to terminate at 30 minutes[3] but the remainder of the procedure did not change.

Five Stage Bleaching

A five stage commercial bleaching sequence (CEDED) was designed for the 12 circulating digester pulps. The bleaching conditions are shown in Table 3.

Each bleaching sequence started with 12 grams of moisture-free pulp charge, and 25% of the pulp was used for a 40 ml permanganate number test (CE-K number) after the E_1 stage, in order to measure the residual lignin contents in the pulps.

Data Analysis

Bomb Cooks

Twenty independent variables (see Appendix 4) were used for the full model multiple regression analysis of the response variables of pulp yield, Kappa number, unbleached brightness, residual alkali, and

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[2] (Continued) Calculation:

$$\frac{(\text{ml of Thiosulfate}) \times (\text{Normality of Thiosulfate}) \times (74.5/2) \times 1000}{\text{ml of NaOCl} \times 1000}$$

$= \text{NaOCl gms/liter}$

[3] In the text this will be called a 30 minute test, while the previously described procedure will be called an exhaustion test.

Table 3. Five-Stage Bleaching Conditions.

	Chemical (%)	Consistency (%)	Temperature °F	Retention (hr)
Chlorination (C)	7	3	25	1
Alkali Extraction (E_1)	3	8	70	2
Chlorine Dioxide (D_1)	1	8	70	3
Alkali Extraction (E_2)	1	8	70	2
Chlorine Dioxide (D_2)	0.5	8	70	3

pH value. An HP 9825 computer was used for the multiple regression analysis and the statistical "t-directed search" (11). This searching procedure first develops the full model with all the 20 potential independent variables. The absolute t* value of each variable was determined as follows:

$$t^* = \frac{b_k}{s(b_k)}$$

where: b_k = estimated coefficient for kth variable

$s(b_k)$ = estimated standard deviation for kth variable

The "t-directed search" test for the best reduced model works as follows: The full regression model (20 X-variables) was calculated, and the t* values for each of the 20 X-variables was examined by the computer. Variables with t* values less than a previously rejection level established (t = 0.5 in the first iteration) were dropped and a new multiple regression equation was then calculated using the remaining X-variables, that is, only the variables whose original t* value exceeded 0.5. The computer examines the newly calculated t* values and rejects those X-variables whose t* values is less than 1.0, a rejection level 0.5 above the original rejection level. This process is reiterated until the rejection t level is 3.0, which typically reduces the number of X-variables to three or less. The first t rejection level of 0.5 and the incremental steps of 0.5 are arbitrary; either or both can be changed to fit a particular regression.

An F (reduced vs. full) test is provided to examine the relative importance of a reduced model to a full model (11).

Ho: All coefficients of the eliminated terms are zero.

Ha: At least one is not zero.

Test Statistic:

$$F\ (\text{reduced vs. full}) = \frac{SSE(R) - SSE(F)}{df(R) - df(F)} \div \frac{SSE(F)}{df(F)}$$

where: SSE(R) = sum of square error of reduced model

SSE(F) = sum of square error of full model

df(R) = degree of freedom of reduced model

df(F) = degree of freedom of full model

Low values of F (reduced vs. full) indicate that the contributions of the eliminated terms to a process is insignificant; high values indicate that the process is relatively sensitive to changes in those variables.

The best way to control a process is to develop a model which accurately relates a set of processing conditions to control of a response variable. While a model with all terms is such a model, it is cumbersome to operate a process by keeping every independent variable in the model. The contributions of some variables could be small and if they can be eliminated from the full model without significantly losing the predictive ability of the regression equation, the controlling procedure can be simplified.

Several criteria can be used to select the best model of a process, such as described by Netter and Wasserman (11).

MSE (mean square error) criterion: A reduced model with the fewest terms having a MSE not significantly higher than the MSE of the full model is considered best.

r^2 (coefficient of determination) criterion: a reduced model with the fewest terms having an r^2 not significantly lower than the r^2 of the full model is considered best.

Cp criterion: Cp is the estimator of total square error.

$$Cp = \frac{SSEp}{MSE} - (n - 2p)$$

where: SSEp = sum square error of the model of interest

MSE = mean square error of full model

n = number of trials

p = number of regression parameters in the model of interest.

When there is no bias in a regression equation with P - 1 independent variables, Cp has an expected value of p. Using this criterion, the reduced model with the smallest Cp value is considered to be the best model.

Circulating Digester Cooks

From the testing results, separate regressions were obtained for AP (aged chip pulp) and FP (fresh chip pulp), respectively. An F* test (11) was used to test whether the two regressions were identical.

The pooled regression function for both pulps can be expressed as follows:

$$E(Y_{ij}) = \beta_{0j} + \beta_{1j}X_{ij} + \beta_{2j}X^2_{ij} \qquad \text{Full model}$$

$$i = 1, \ldots, n_j; \quad j = 1, 2$$

when j = 1, the first regression (AP):

$$E(Y_{i1}) = \beta_{01} + \beta_{11}X_{i1} + \beta_{21}X^2_{i1}$$

$$i = 1, \ldots, n_1$$

when j = 2, the second regression (FP):

$$E(Y_{i2}) = \beta_{02} + \beta_{12}X_{i2} + \beta_{22}X^2_{i2}$$

$$i = 1, \ldots, n_2$$

$$SSE\text{ (full model)} = SSE_1 + SSE_2$$

where:

SSE (full model) = sum square error of the pooled model.

SSE_1 = sum square error of the first regression

SSE_2 = sum square error of the second regression.

$$E(Y_{ij}) = \beta_0 + \beta_1 X_{ij} + \beta_2 X^2_{ij} \qquad \text{Reduced model}$$

$$i = 1, \ldots, n_j; \quad j = 1, 2$$

SSE (reduced model) = sum of square error of the reduced model.

Ho: $\beta_{01} = \beta_{02}$ and $\beta_{11} = \beta_{12}$ and $\beta_{21} = \beta_{22}$

Ha: not Ho

Test Statistics:

$$F^* = \frac{\text{SSE (reduced model)} - \text{SSE (full model)}}{(n_1 + n_2 - 2) - (n_1 + n_2 - 4)} \div \frac{\text{SSE (full model)}}{n_1 + n_2 - 4}$$

where: n_1 = degrees of freedom of the first regression

n_2 = degrees of freedom of the second regression

At a significance level α:

If $F^* < F(1 - \alpha;\ 2,\ n_1 + n_2 - 4)$, Ho is accepted, and there is no difference between these two regressions.

If $F^* > F(1 - \alpha;\ 2,\ n_1 + n_2 - 4)$, the differences exist between these two regressions.

Wood Identification

Wood fibers (pulps) were identified under a microscope (100X). Douglas-fir fibers (tracheids) can be distinguished from the others by the spiral thickenings in the inner walls of the tracheids. The percentages of Douglas-fir in the aged chips and fresh chips were reported as the average of numbers of Douglas-fir fibers in every 100 fibers counted.

RESULTS AND DISCUSSION

Wood Analyses

The results of wood analyses are given in Table 4.

Table 4. Results of Wood Analyses

Subjects	Fresh Chips	Aged Chips
1% NaOH solubility	16.21%[a]	19.61%
Alcohol/Benzene extraction	5.21%	2.44%
Hot water extraction	1.95%	0.77%
Holocellulose content	67.04%	64.63%
Klason lignin	26.37%	31.39%
1% CUENE[b] viscosity (centipoises)	101	44
pH value[c]	3.73	3.58

[a]All the percentages are based on the o.d. specimen.
[b]CUENE is cupriethylenediamine.
[c]pH value of distilled water is 5.47.

One Percent Caustic Soda Solubility

TAPPI Standard T 4m-59 states: "As the wood decays, the percentage of alkali-soluble material increases, and the pulp yield, as a result of the decay, decreases."

During outdoor chip storage, a combination of physiological, microbial, and chemical reactions cause heating of the pile, which will do severe damage to the wood chips. The severity of degradation is proportional to the storage period, the amount of heating, and the extent of microbial attack. A long period of outdoor storage could cause substantial damage to the wood, leaving lower molecular weight polysaccharides and smaller molecular fragments of lignin (9, 10). Therefore, the amount of alkali-soluble extractives increases. The increase in one percent alkali solubility can be used as a basis for measuring a rot index for decayed chips (10).

The original sources of fresh chips and aged chips which were utilized in this study were different. However, they were assumed to have about the same chemical compositions when both of them were fresh and undegraded.

The results in Table 4 show that aged chips have higher alkali solubility in one percent NaOH than fresh chips.

Alcohol-Benzene Solubility

Some of the extractives in wood such as the terpenes are volatile. If the wood is stored as chips rather than as logs, the increased specific surface enables the volatile substances to evaporate more rapidly. The longer the storage time, the lower the extractive content should be.

Table 4 shows that the 5.2% alcohol-benzene solubility for fresh chips is more than double the 2.4% extractive content for aged chips, confirming the above hypothesis.

The extractive substances may be located in the cell lumens, middle lamella, pit cavities or pit membranes. This may either block or decrease the penetration rate of cooking liquor. Therefore, a lower extractive content wood might be pulped much easier than a higher extractive content wood.

Hot Water Solubility of Wood

The results in Table 4 show that fresh chips have higher solubility in hot water than aged chips. Some of the water-soluble materials were probably leached out of the wood chips during the aging process.

Holocellulose in Wood

Some holocellulose may be degraded to lower molecular weight components during the aging process in a chip pile. These components might be attacked and leached out during $NaClO_2$ treatment, although $NaClO_2$ preferentially attacks lignin.

Table 4 shows that the holocellulose content in aged chips is lower than that in fresh chips.

Lignin in Wood

During storage some kind of fungi will digest certain amounts of carbohydrates and leave most of the lignin in the wood, thus causing the lignin content to be relatively increased. Table 4 shows that the lignin content in aged chips is higher than that in fresh chips.

A wood with higher lignin content should result in a lower pulp yield at the same Kappa number; this is one of the most serious disadvantages of aged chips.

Viscosity

The falling ball method is used in determining the viscosity of the holocellulose. Table 4 shows that aged chips have lower viscosity (lower degree of polymerization) implying that they are much more degraded than fresh chips.

pH Value in Wood

Table 4 shows the acidity of aged chips is higher than that of fresh chips, but the difference is small.

Conclusion

Conventionally, we know that a degraded wood should have higher alkali solubility but lower extractives, lower viscosity, and lower pH value when compared with a sound wood. The results of the wood analysis confirm these expectations. However, changes in lignin and holocellulose during the degradation process depend on the conditions of degradation and types of microorganisms involved. In this case, there was a loss of holocellulose and a relative gain in lignin during degradation.

Results of Bomb Cooks

The original data are listed in Appendix 1.

Pulp Yield

A "t-directed search" (11) statistical analysis for pulp yield is shown in Appendix 5. The reduced model at rejection level t = 1.50

with $r^2 = 0.97$ and Cp = 4.0 is assumed to be the best model, which is shown in Table 5.

A strong correlation exists between pulp yields and the six-variable reduced model. Chemical charge is the most significant variable and it has a strong negative effect on pulp yield.

From the best model regression equation in Table 5, three reduced equations can be obtained by holding the variables of time, temperature and sulfidity at their central value (= 3) but with chip ratio levels 1, 3 and 5 (0 - 100%, 50 - 50% and 100 - 0% fresh-aged chip ratios).

The reduced equations:

(1) Chip-ratio = 1 (100% fresh chips)

$$\text{Pulp yield} = 84.62 - 18.46\,(\text{chemical}) + 2.19\,(\text{chemical})^2$$

(2) Chip-ratio = 3 (50 - 50% of fresh-aged blended chips)

$$\text{Pulp yield} = 80.82 - 18.46\,(\text{chemical}) + 2.19\,(\text{chemical})^2$$

(3) Chip-ratio = 5 (100% aged chips)

$$\text{Pulp yield} = 76.82 - 18.46\,(\text{chemical}) + 2.19\,(\text{chemical})^2$$

These three equations were used to calculate the yield values shown in Figure 1A.

Results show that when the variables of time, temperature and sulfidity were held at their central conditions, the pulp yield decreases as the percentage of aged chip increases, and that the yield decreases as the chemical charge increases.

Kappa Number

The best regressed model, shown in Table 6, was selected from Appendix 6 at t = 1.5, which has $r^2 = 0.95$, Cp = 0.24.

Table 5. Multiple Regression of Bomb Cooking Variables on Pulp Yield - Best Model.

t = 1.5 rejection level	ANOVA	$r^2 = 0.97$ F (reduced vs. full) = 0.36

Source	DF	SS	MS	F
Regression	9	1101.29	183.55	158.85
Error	26	30.04	1.16	
Total	32	1131.33		

Term[a]	Coefficient	t*-Value
Constant	97.07	
Time	- 1.04	- 4.75
Temperature	- 2.46	-11.20
Chemical	-19.81	-16.22
$(\text{Chemical})^2$	2.19	11.28
(Chemical) · (Sulfidity)	0.45	4.77
(Sulfidity) · (Chip Ratio)	- 0.65	- 9.56

[a]See Table 1.

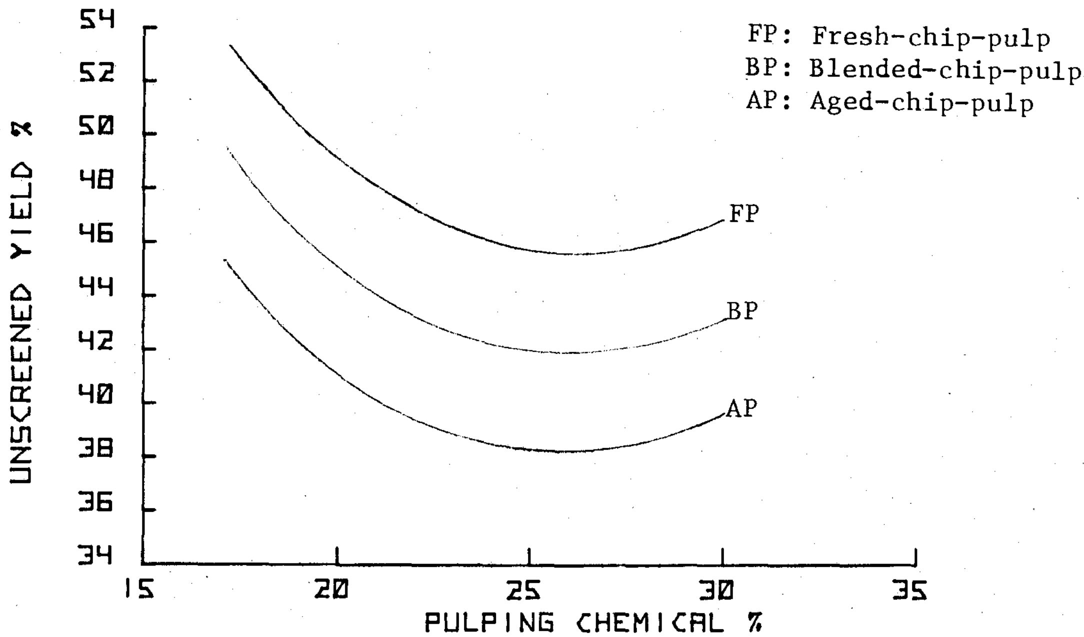

Figure 1A. Parameter lines of unscreened pulp yield vs. chemical charge with the remaining variables at their central level. (Prediction from the best model in Table 5.)

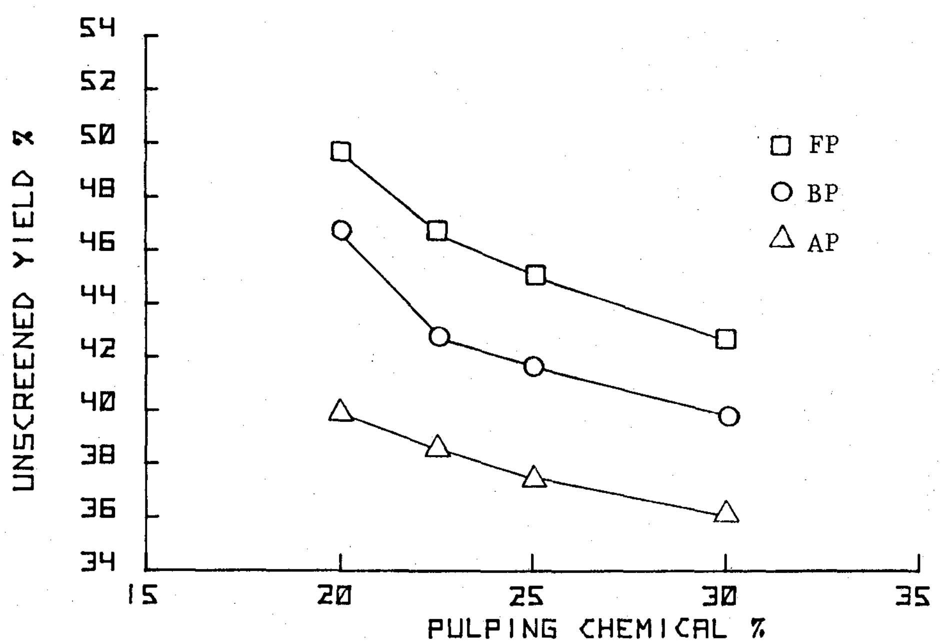

Figure 1B. Unscreened pulp yield vs. chemical charge —— Circulating digester cooks.

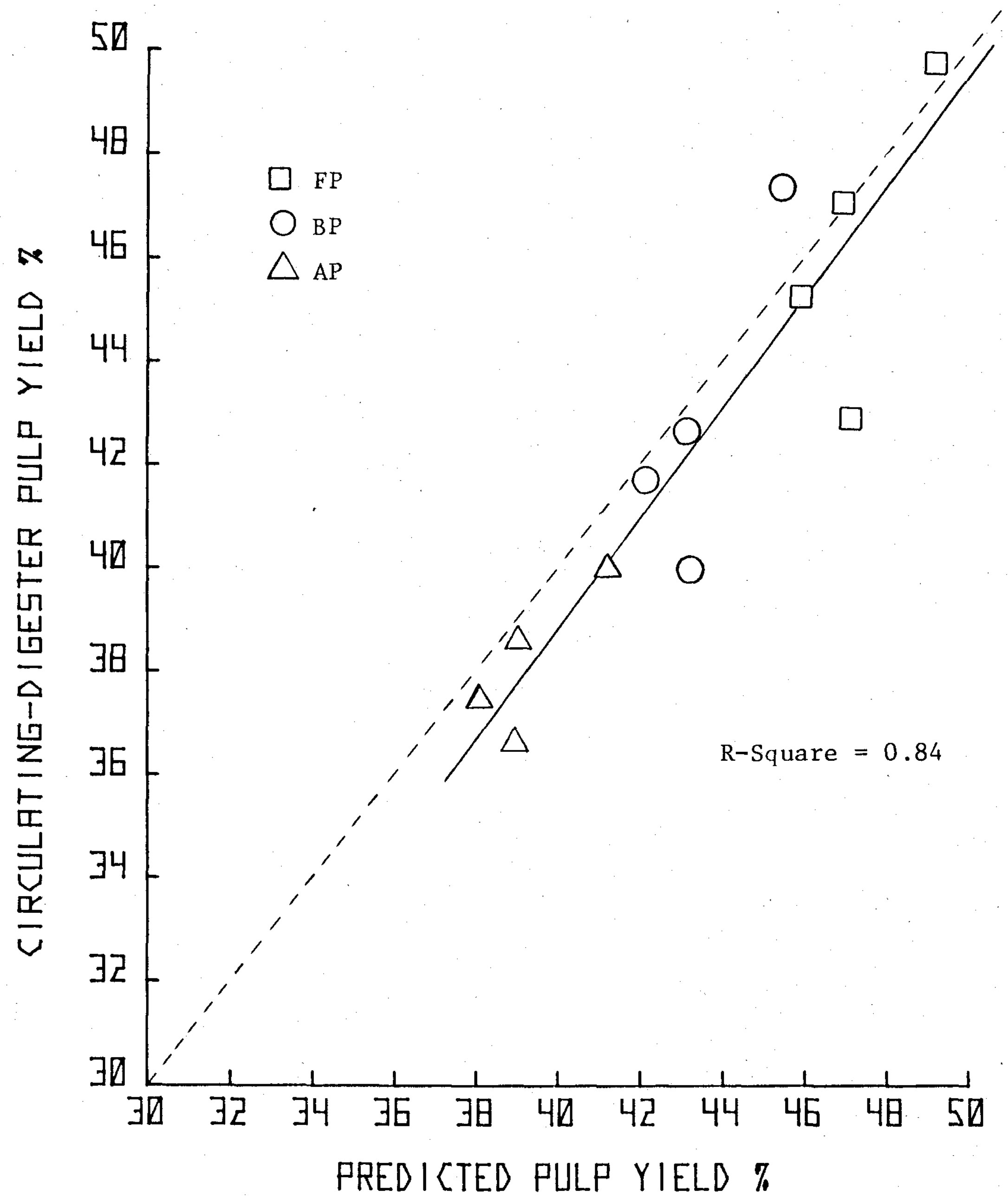

Figure 2. Unscreened pulp yield of circulating digester cook vs. predicted values from the best model in Table 5.

Table 6. Multiple Regression of Bomb Cooking Variables on Kappa Number - Best Model.

t = 1.5 rejection level   ANOVA $r^2 = 0.95$
F (reduced vs. full) = 0.44

Source	DF	SS	MS	F
Regression	8	19853.82	2481.73	62.10
Error	24	959.15	39.96	
Total	32	20812.97		

Term[a]	Coefficient	t*-Value
Constant	280.40	
Time	-20.28	-2.90
Temperature	-29.53	-4.22
Chemical	-54.86	-7.84
Sulfidity	- 4.12	-3.20
Chip Ratio	- 3.79	-2.94
$(Time)^2$	2.61	2.28
$(Temperature)^2$	3.23	2.82
$(Chemical)^2$	4.98	4.35

[a]See Table 1.

A strong relationship is seen between Kappa number and the first order term of the five variables, which are negatively correlated to Kappa number.

Similar to the derivation of reduced regression equations for pulp yield, three equations related to Kappa number are shown as follows:

(1) Chip ratio = 1 (100% fresh chips)

Kappa number = 167.38 - 54.86 (chemical) + 4.98 $(\text{chemical})^2$

(2) Chip ratio = 3 (50 - 50% of fresh-aged blended chips)

Kappa number = 159.80 - 54.86 (chemical) + 4.98 $(\text{chemical})^2$

(3) Chip ratio = 5 (100% of aged chips)

Kappa number = 152.22 - 54.86 (chemical) + 4.98 $(\text{chemical})^2$

Figure 3A shows that the Kappa number of aged-chip pulp (AP) is lower than that of fresh-chip pulp (FP) when the variables of time, temperature and sulfidity are held constant at their central control condition.

Unbleached Pulp Brightness

The statistical "t-directed search" data for unbleached brightnesses are given in Appendix 7.

A reduced model at rejection level t = 1.50 was assumed to be the best, shown in Table 7, which has $r^2 = 0.96$ without a significant drop from the full model ($r^2 = 0.97$), and a Cp value of 5.98.

Chemical charge was found to be the most significant variable in the reduced model. Similar to the method previously described, reduced regression equations were derived as follows:

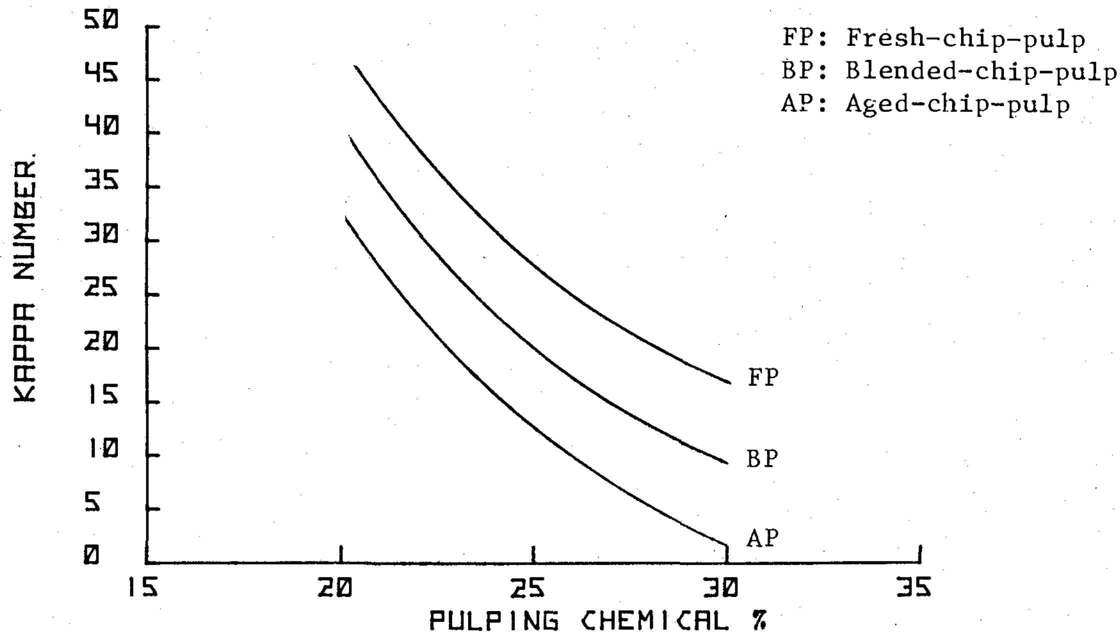

Figure 3A. Parameter lines of Kappa number vs. chemical charge with the remaining variables at their central level. (Prediction from the best model in Table 6.)

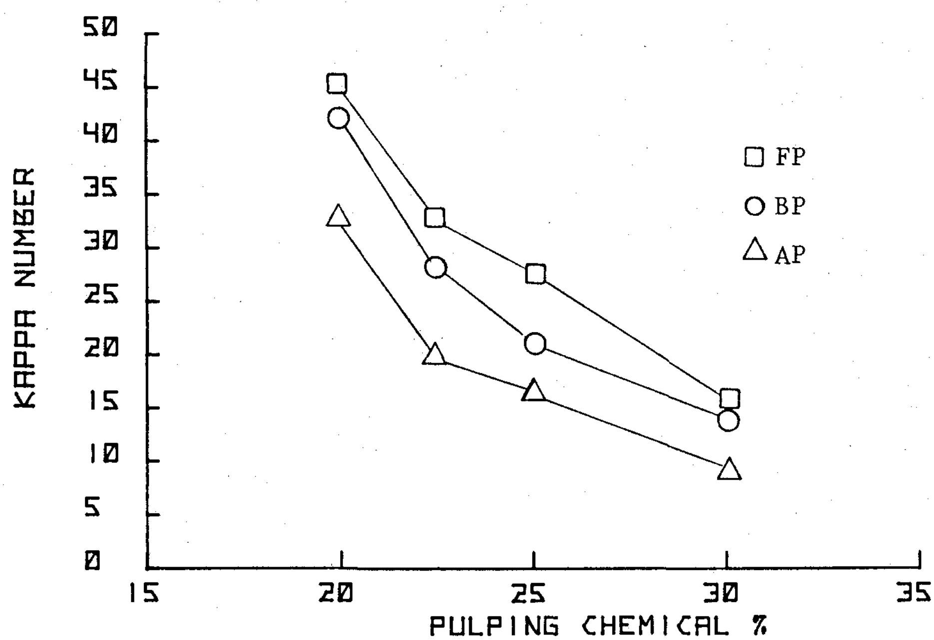

Figure 3B. Kappa number vs. chemical charge — Circulating digester cooks.

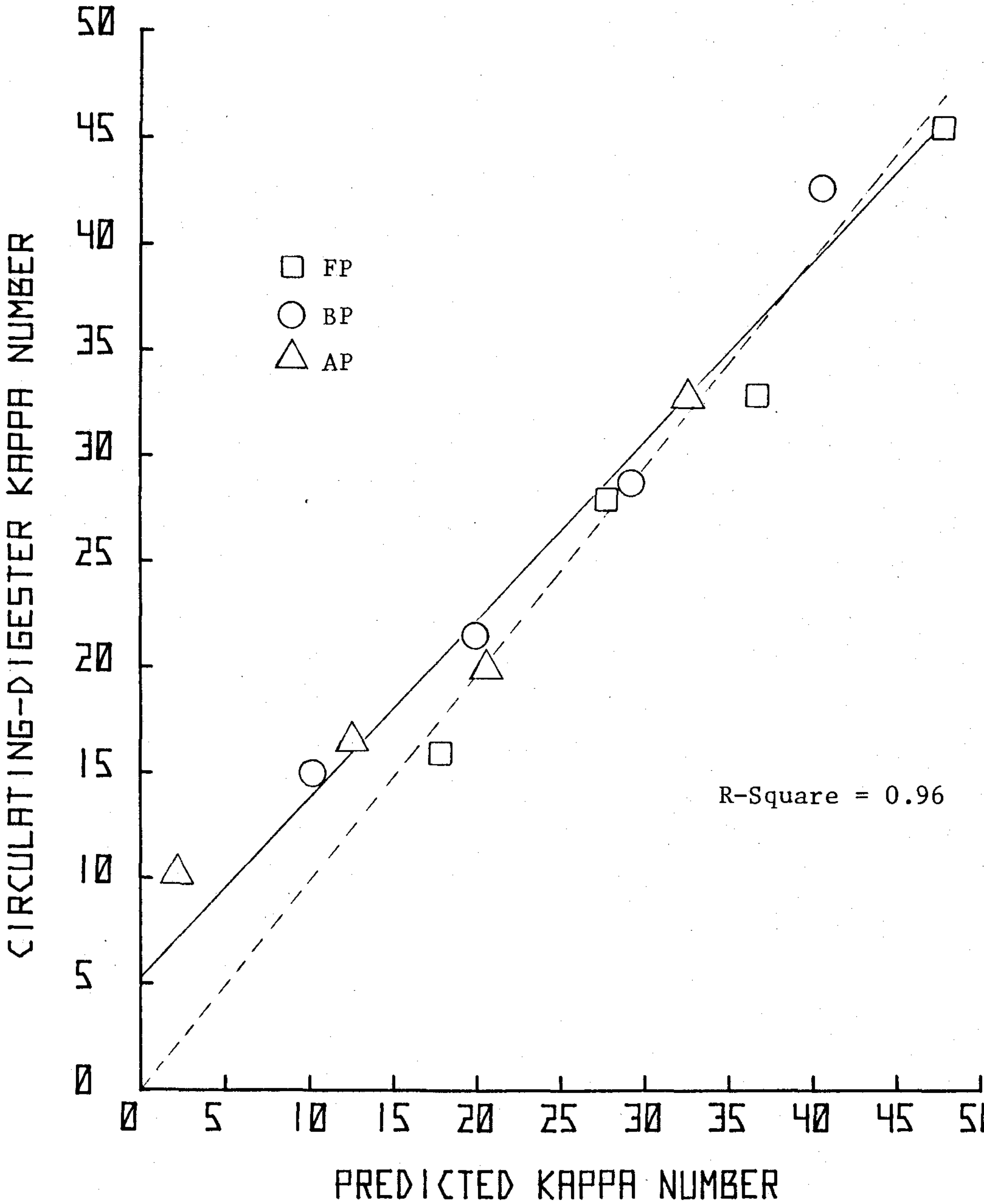

Figure 4. Kappa number of circulating digester pulp vs. predicted values from the best model in Table 6.

Table 7. Multiple Regression of Bomb Cooking Variables on Unbleached Pulp Brightness - Best Model.

t = 1.5 rejection level	ANOVA	$r^2 = 0.96$ F (reduced vs. full) = 0.82

Source	DF		MS	F
Regression	9	986.45	109.61	54.75
Error	23	46.05	2.00	
Total	32	1032.50		

Term[a]	Coefficient	t*-Value
Constant	-11.21	
Time	0.75	2.60
Temperature	3.13	1.44
Chemical	8.85	4.68
Sulfidity	1.95	1.78
$(\text{Temperature})^2$	- 0.34	-1.33
(Temperature) • (Chemical)	0.64	1.80
(Temperature) • (Sulfidity)	- 0.49	-1.38
$(\text{Chemical})^2$	- 0.79	-3.08
$(\text{Chip Ratio})^2$	0.09	1.80

[a]See Table 1.

(1) Chip-ratio = 1 (100% fresh chips)

Unbleached pulp brightness =

$$- 1.10 + 10.77 \text{ (Chemical)} - 0.79 \text{ (Chemical)}^2$$

(2) Chip-ratio = 3 (50 - 50% of fresh-aged blended chips)

Unbleached pulp brightness =

$$-0.38 + 10.77 \text{ (Chemical)} - 0.79 \text{ (Chemical)}^2$$

(3) Chip-ratio = 5 (100% aged chips)

Unbleached pulp brightness =

$$1.06 + 10.77 \text{ (Chemical)} - 0.79 \text{ (Chemical)}^2$$

The parameter lines of Figure 5A were drawn according to the reduced equations.

For the same pulping condition, the unbleached brightness of AP is superior to FP, though no by very much. A statistical t*-test (11) was made as follows:

Ho: The unbleached brightness is no different between AP and FP.

Test statistic:

$t^* = 1.8$ (from Table 7).

(1) For level of significance = 0.05

$t^* < t\ (0.975;\ 23) = 2.069$ (11)

Therefore, Ho is accepted.

(2) For level of significance = 0.10

$t\ (0.95;\ 23) = 1.714 < t^*$

Therefore, we reject Ho, and the difference exists.

Pulp Yields vs. Kappa Number

There is a linear relation ($r^2 = 0.82$) between pulp yields and

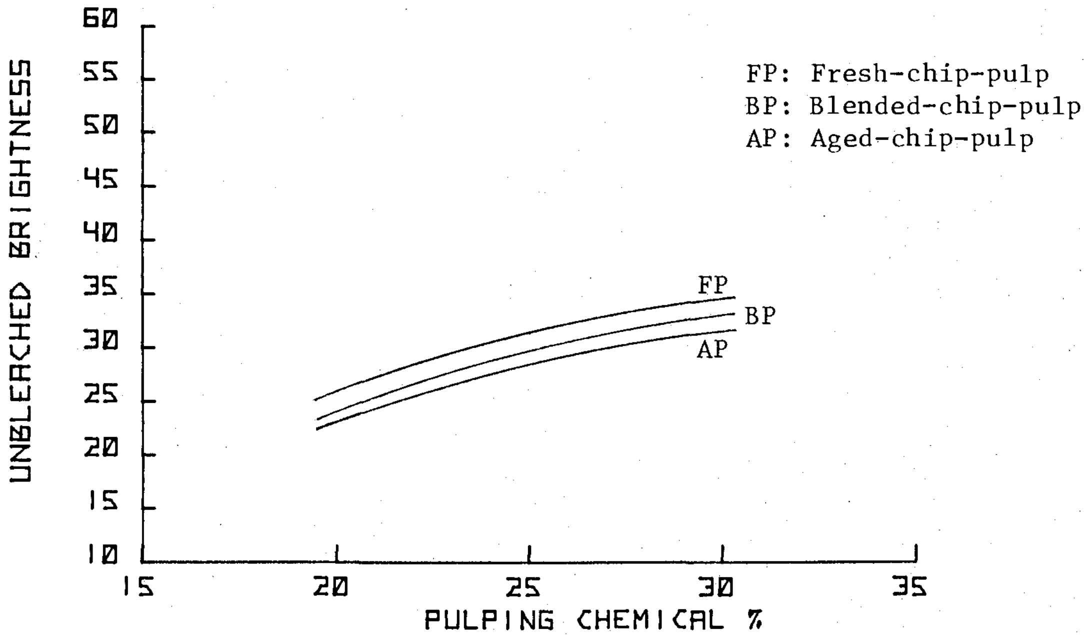

Figure 5A. Parameter lines of unbleached pulp brightness vs. chemical charge with the remaining variables at their central level. (Prediction from the best model in Table 7.)

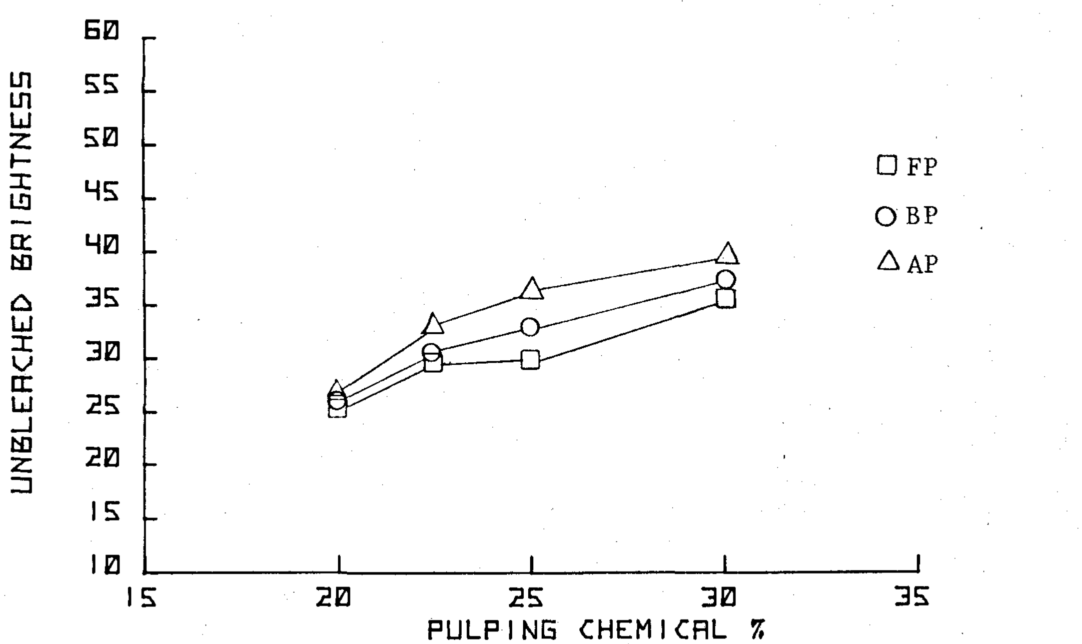

Figure 5B. Unbleached pulp brightness vs. chemical charge — Circulating digester cooks.

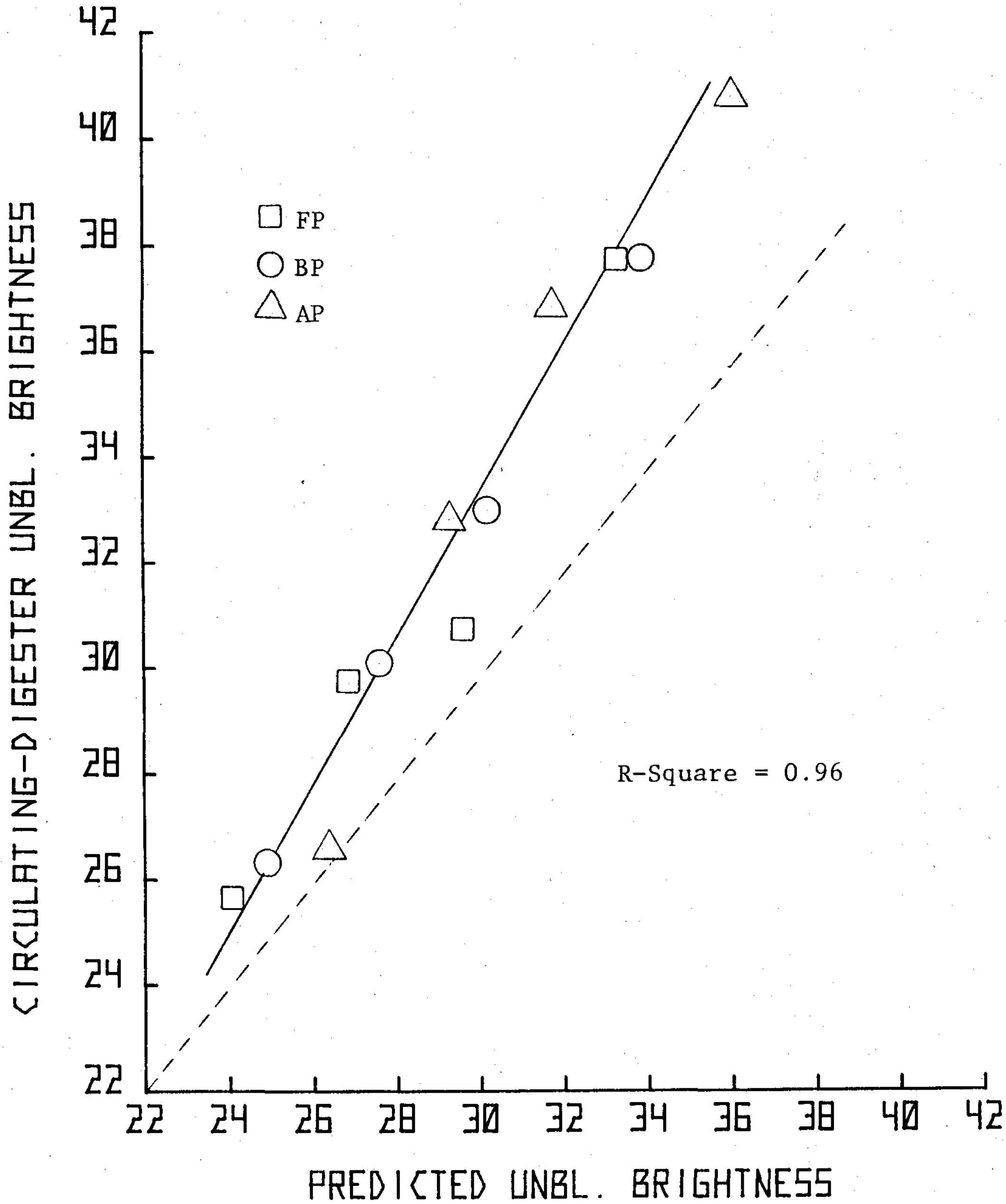

Figure 6. Unbleached brightness of circulating digester pulp vs. predicted values from the best model in Table 7.

Kappa number as shown in Figure 7A. When the chips were pulped to low Kappa numbers, the carbohydrates in wood were also degraded and leached out as well as lignin, and this resulted in low pulp yields. Therefore, Kappa numbers can be used as an index to predict the pulp yields. However, in this case the effects of aged wood on the pulp yields were not shown, because there was a co-variation in the five pulping parameters that may cause interaction effects. Considering the interactions of the five variables, the linear relationship is a good model for this system.

Unbleached Pulp Brightness vs. Kappa Number

The results of a linear regression analysis between unbleached pulp brightness and Kappa number are given in Table 8, and the regression line is shown in Figure 8A.

Table 8. Linear Regression of Unbleached Pulp Brightness Against Kappa Number.

ANOVA $r^2 = 0.95$

Source	DF	SS	MS	F
Regression	1	978.83	978.83	565.31
Error	31	53.67	1.73	
Total	32	1032.50		

Term	Coefficient
Constant	34.44
Kappa Number	-0.22

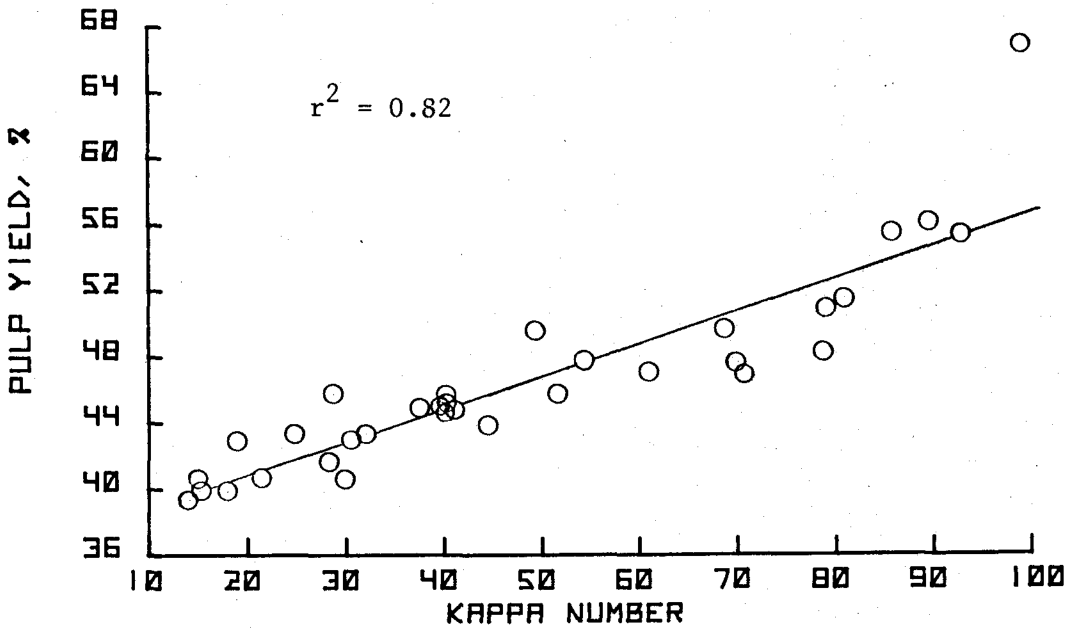

Figure 7A. Unscreened pulp yield vs. Kappa number — Bomb cooks.

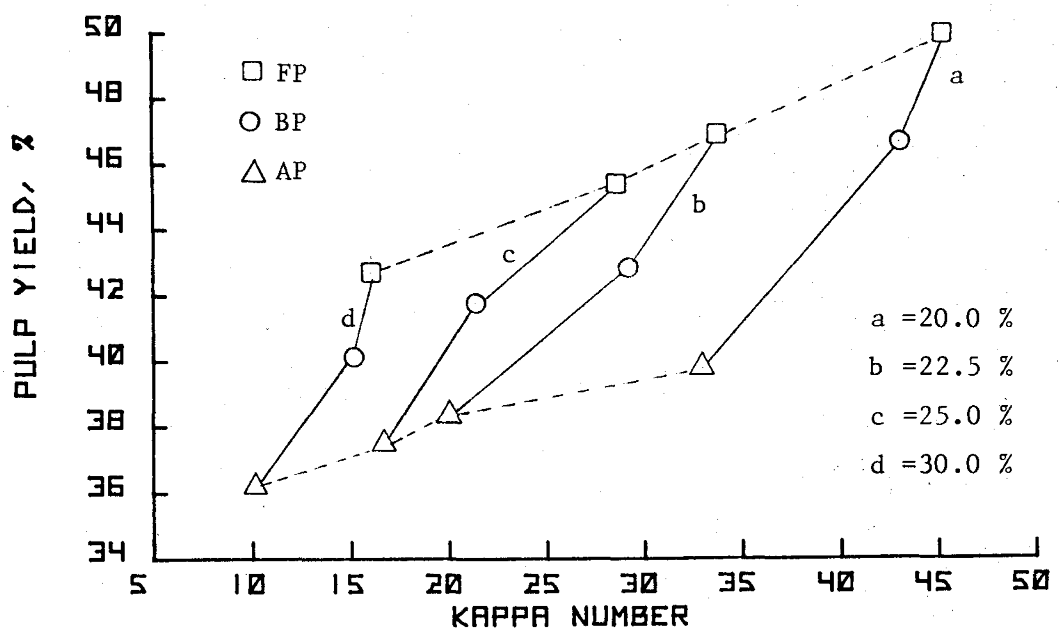

Figure 7B. Unscreened pulp yield vs. Kappa number — Circulating digester cooks.

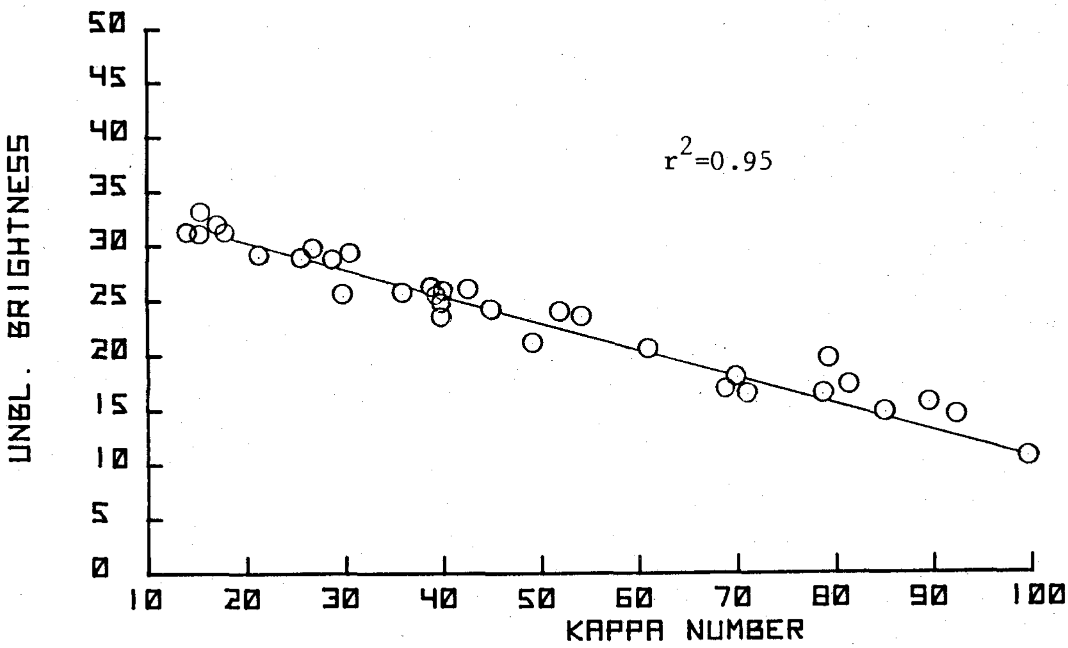

Figure 8A. Unbleached pulp brightness vs. Kappa number — Bomb cooks.

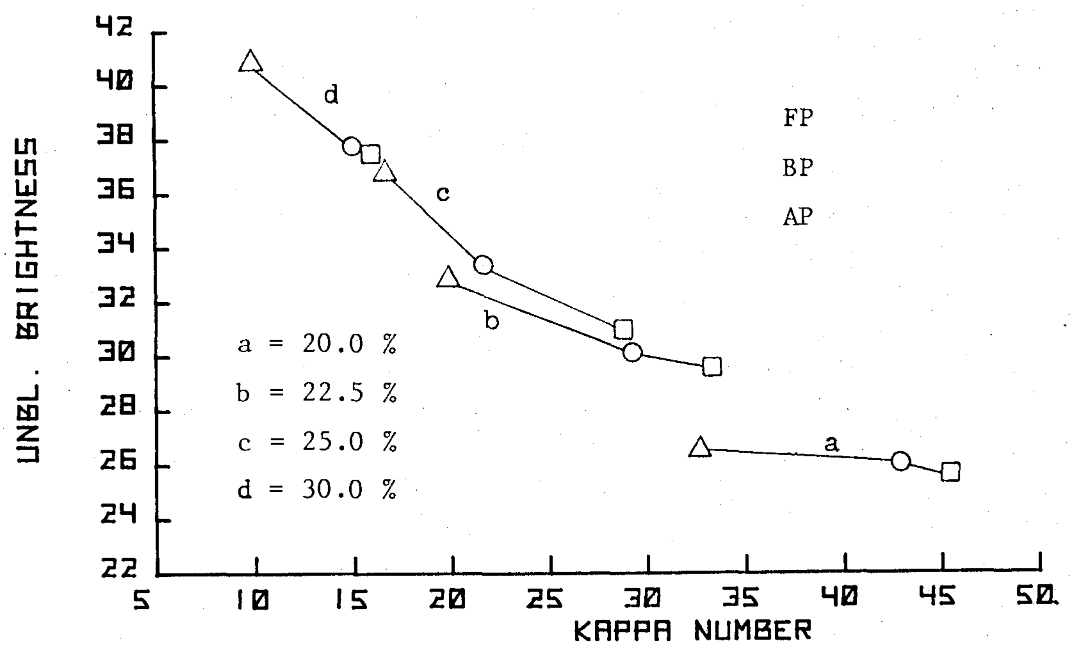

Figure 8B. Unbleached pulp brightness vs. Kappa number — Circulating digester cooks.

Single Stage Bleached Brightness vs. Kappa Number

A good relationship between single stage bleached pulp brightness and Kappa number was found, as shown in Table 9 and Figure 9A (4% NaOCl charge); Table 10 and Figure 9B (8% NaOCl charge).

The bleached pulp brightness at the two different bleaching chemical charges are highly correlated with Kappa number. However, the 8% NaOCl charge relationship with $r^2 = 0.96$ is superior. The higher chemical charge might overshadow instrumental and operator errors.

Residual Alakli in Waste Liquor

The statistical data are given in Appendix 8. A two-variable reduced model at rejection level t = 3.0 was found to be the best, with an $r^2 = 0.97$, and a low F (reduced vs. full) value. Most important is the fact that the process can be controlled by only two variables: chemical charge and sulfidity.

All the terms associated with the chip ratio variables were dropped out at t = 2.50. A reduced model at t = 2.0 shown in Table 11 indicates that the chip ratio has a negative effect, meaning that the higher content of aged chips, the greater amount of alkali will be consumed.

pH of Waste Liquor

The statistical t-directed search analysis is given in Appendix 9. The best model is shown in Table 12. The results show that the pH value is strongly affected by the chemical charge. The presence of aged chips lowers the pH of the waste liquor when the variables of time, temperature and sulfidity are held at their central conditions.

Table 9. Polynomial Regression of 4 % NaOCl Bleached Pulp Brightness Against Kappa Number.

ANOVA $r^2 = 0.94$

Source	DF	SS	MS	F
Regression	2	6112.255	3056.127	248.474
Error	30	368.988	12.299	
Total	32	6481.242		

Term	Coefficient
Constant	74.445
Kappa Number	-1.219
$(\text{Kappa Number})^2$	0.007

Table 10. Polynomial Regression of 8 % NaOCl Bleached Pulp Brightness Against Kappa Number.

ANOVA $r^2 = 0.96$

Source	DF	SS	MS	F
Regression	2	12092.357	6046.179	390.275
Error	30	464.763	15.492	
Total	32	12557.120		

Term	Coefficient
Constant	96.076
Kappa Number	-1.379
$(\text{Kappa Number})^2$	0.006

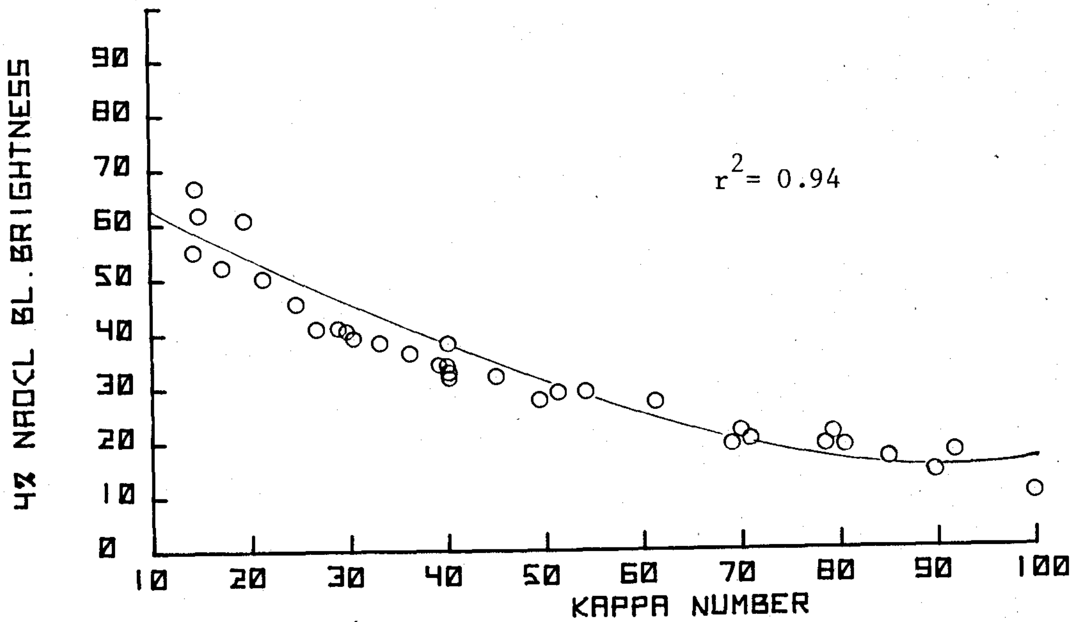

Figure 9A. 4% NaOCl bleached brightness vs. Kappa number of unbleached pulp — Bomb cooks.

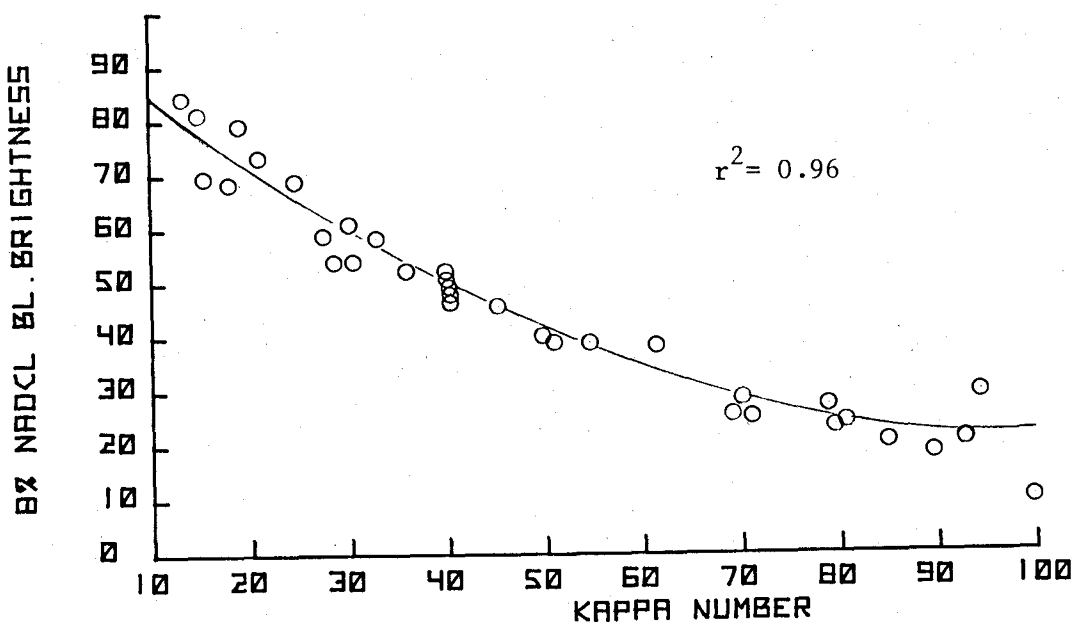

Figure 9B. 8% NaOCl bleached brightness vs. Kappa number of unbleached pulp — Bomb cooks.

Table 11. A Reduced Regression Model of Bomb Cooking Variables on Residual Alkali.

t = 2.0 (rejection level) ANOVA $r^2 = 0.98$
F (reduced vs. full) = 1.1

Source	DF	SS	MS	F
Regression	5	725.72	145.14	284.85
Error	27	13.76	0.51	
Total	32	739.48		

Term[a]	Coefficient	t*-Value
Constant	-4.84	
Chemical	5.83	28.81
Chip Ratio	-0.22	-1.52
(Time) • (Sulfidity)	-0.05	-1.00
(Temperature) • (Chemical)	-0.13	-2.87
Sulfidity	0.14	4.29

[a]See Table 1.

Table 12. Multiple Regression of Bomb Cooking Variables on pH of Waste Liquor.

t = 2.0 (rejection level) ANOVA $r^2 = 0.93$
F (reduced vs. full) = 0.49

Source	DF	SS	MS	F
Regression	9	17.38	1.93	34.19
Error	23	1.30	0.06	
Total	32	18.68		

Term[a]	Coefficient	t*-Value
Constant	9.89	
Time	-0.87	-5.20
Chemical	2.22	7.31
(Time) · (Temperature)	0.14	3.44
(Time) · (Chip Ratio)	0.13	3.33
(Temperature) · (Sulfidity)	-0.14	-3.54
$(\text{Chemical})^2$	-0.31	-7.25
(Chemical) · (Sulfidity)	0.13	2.42
$(\text{Sulfidity})^2$	0.07	2.30
(Sulfidity) · (Chip Ratio)	-0.15	-3.65

[a]See Table 1.

Conclusions

1. For the same pulping conditions, AP (aged chip pulp) has lower Kappa numbers, lower pulp yields, but higher unbleached brightnesses than FP (fresh chip pulp). The interpretation is that the degraded wood in the aged chips dissolves quite rapidly in the alkaline pulping liquor and leaves less good pulp.

2. The unbleached pulp brightness is highly correlated with the Kappa number. The higher the Kappa numbers, the lower the brightness, and vice versa.

3. With the same amount of chemical charge in the single stage bleachability test, a higher bleached brightness can be obtained from a lower Kappa number pulp. A good relationship exists between bleached brightness and the Kappa number of the unbleached pulp.

4. It was found that the pH of the aged chips was lower than that of the fresh chips, and this may explain the lower pH of the waste liquors from aged chip pulping.

5. For the same pulping condition, more alkali will be consumed by aged chips than by fresh chips.

6. Chemical charge was found to be the most important variable for controlling the response variables of pulp yield, Kappa number, unbleached pulp brightness, etc. Therefore, it was chosen to be the only controlling variable for the circulating digester cooks.

Results of Circulating Digester Cooks

The results of the circulating digester cooks are given in Appendix 2.

Pulp Yields

The 12 data points for the pulping yields are shown in Figure 1B plotted against chemical charge.

As the chemical charge increases, the pulp yield decreases. For the same pulping conditions, the pulp yields of AP were about 7 to 10% lower than FP. This reveals that a degraded wood can be more easily dissolved by alkali than a sound wood, which results in lower yields for degraded wood chips. The low pulp yield is one of the worst disadvantages of degraded wood. In this case, it would take about 20% more aged chips to produce the same amount of pulp than fresh chips.

In Figure 2, the dotted line which passes through the origin point with a slope equal to one is a hypothetical line, on which the circulating digester pulp yields are exactly the same as the values predicted from the results of the bomb cooks (see Appendix 10). Since the bombs and the circulating digester are different mechanical devices, the deviation might exist. However, with $r^2 = 0.84$ and $F = 51.03$, the regression equations from the bomb cooks are valid for calculating the yields of the circulating digester cooks.

Kappa Number

Figure 3B shows that the higher the chemical charge, the more lignin will be extracted, leading to a lower Kappa number pulp. For the same pulping conditions, the Kappa number of AP is significantly lower than that of FP, implying that the lignin in aged chips might have lower molecular weight than in fresh chips. The low molecular weight lignin can be attacked by alkali more readily, and results in lower lignin content pulp.

Figure 4 indicates that the Kappa numbers of the circulating digester pulps are highly correlated with the predicted Kappa numbers (see Appendix 10) ($r^2 = 0.96$), but the circulating digester pulps tend to have slightly higher Kappa numbers than the predicted values.

Unbleached Pulp Brightness

The unbleached pulp brightnesses of AP, BP, and FP at different levels of pulping chemicals are given in Appendix 2 and shown in Figure 5B. The results show that as the chemical charge increases, the unbleached pulp brightness goes up.

A statistical F*-test (11) was made in order to evaluate the degree of difference of unbleached brightness between AP and FP.

(1) Only the first order term was applied:

$$4.32 = F\ (0.90;\ 2,\ 4) < F^* = 4.7 < F\ (0.95;\ 2,\ 4) = 6.94$$

At $\alpha = 0.05$, there is no difference of unbleached pulp brightness between AP and FP.

At $\alpha = 0.10$, the unbleached brightness of AP is superior to that of FP.

(2) If the first order term and quadratic term were involved then

$$F^* = 43.77 > F\ (0.99;\ 2,\ 4) = 18.0$$

There is a significant difference between AP and FP in the unbleached pulp brightness.

Similar to Figure 2 and Figure 4, Figure 6 shows there is a strong linear relationship ($r^2 = 0.96$) between circulating digester unbleached pulp brightnesses and the predicted values from bomb cooks (see Appendix 10).

During the aging process, both the carbohydrates and lignin in wood might be degraded to lower molecular weight fragments. These may contribute to the higher alkali consumption, compared to undegraded wood (10, 18), which was proven by examining the data of the residual alkali in the waste liquors. Therefore, at the same pulping condition, a significantly degraded wood will result in a pulp with lower yield, lower Kappa number, but higher unbleached brightness than a pulp from undegraded wood.

Relation Between Pulp Yield and Kappa Number

The four separate solid lines shown in Figure 7B represent four different levels of pulping chemical charge. They show that at the same pulping conditions, AP has lower Kappa numbers and lower pulp yields than FP. The dotted lines connect the data points of AP and FP, respectively. At the same Kappa number, AP has significantly lower yield than FP, which is an important consideration for the pulp mill.

Relation Between Unbleached Pulp Brightness and Kappa Number

Similar to Figure 7B, four solid lines shown in Figure 8B represent four different levels of pulping chemical charge. At the same pulping conditions, AP has lower Kappa numbers but higher unbleached brightnesses. At the same Kappa number, FP is slightly superior to AP.

An F*-test (11) shows the following:

(1) Only the first order term was applied:

$4.32 = F(0.90;\ 2, 4) < F^* = 4.85 < F(0.95;\ 2, 4) = 6.94$

(2) Quadratic term was involved as well as the first order term:

$4.32 = F(0.90;\ 2, 4) < F^* = 5.13 < F(0.95;\ 2, 4) = 6.94$

Statistical conclusion: If significance level $\alpha = 0.05$, at the same Kappa number there is no significant difference between the unbleached pulp brightnesses of FP and AP. However, at $\alpha = 0.10$, the unbleached pulp brightness of FP is superior to that of AP.

Single Stage Bleachability Test

The results of the bomb digester pulps single stage bleaching tests show that both 4% and 8% NaOCl bleachabilities are highly correlated with Kappa numbers. However, for the circulating digester pulps, 6% NaOCl was chosen for the bleachability test as the TAPPI Useful Method suggested.

The results of the exhaustion tests (bleaching chemical is consumed completely) and 30-minute tests are listed in Appendix 2. Both of the tests show good relationships between bleached pulp brightnesses and Kappa numbers (Figure 10A, Figure 10B). Results show taht there is no significant difference between the single stage bleaching responses of AP and FP. The bleached pulp brightnesses are highly correlated with Kappa numbers.

Five Stage Bleached Brightness

The original data of five stage (CEDED, see Table 3) bleached

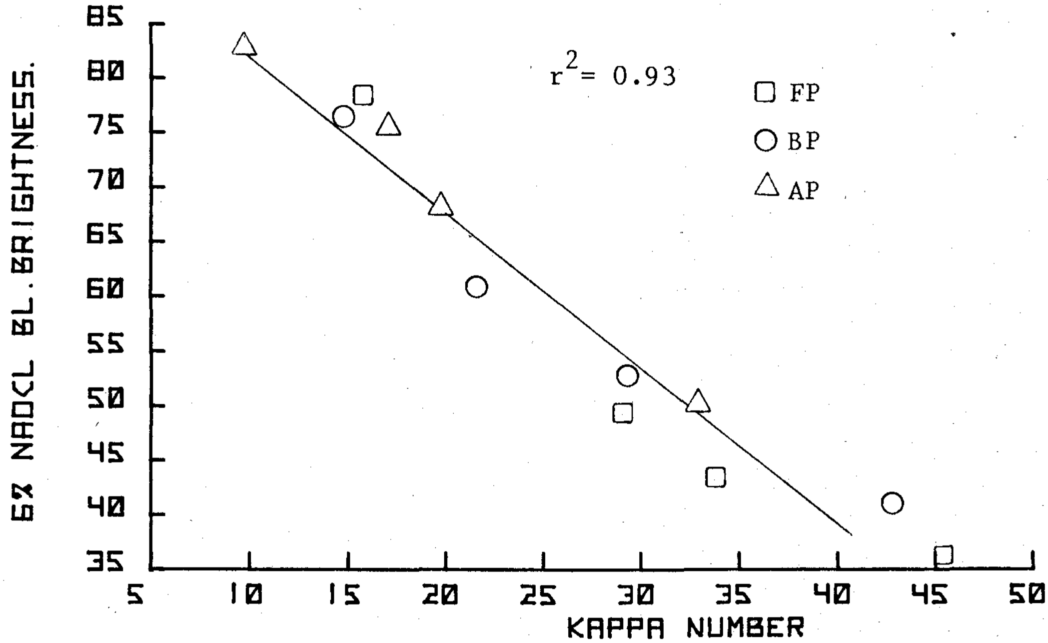

Figure 10A. 6% NaOCl bleached brightness (exhaustion test) vs. Kappa number of unbleached pulp — Circulating digester cooks.

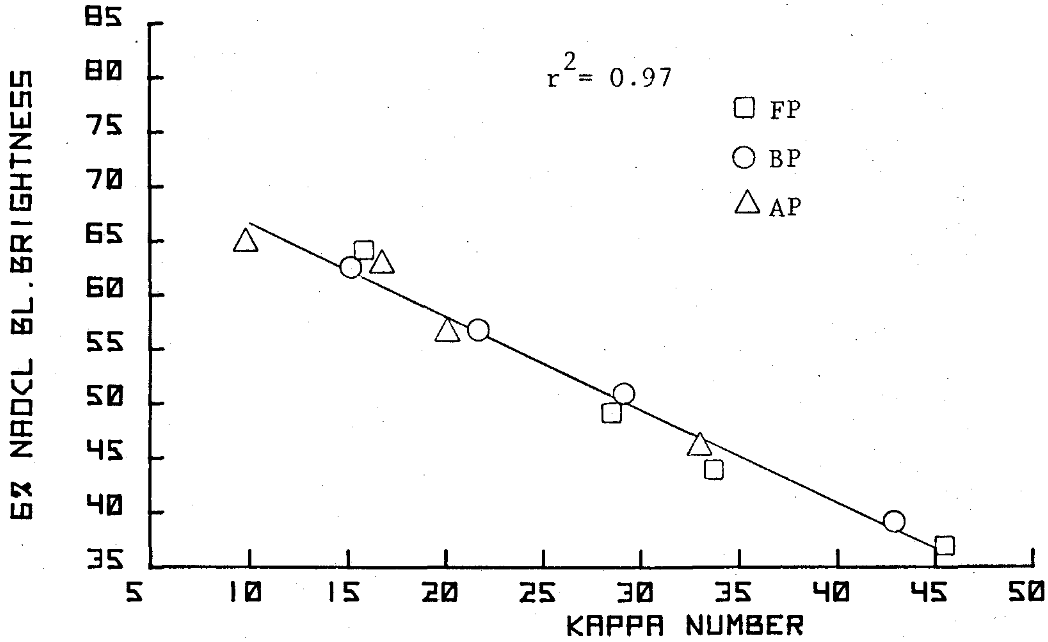

Figure 10B. 6% NaOCl bleached brightness (30 minute test) vs. Kappa number of unbleached pulp — Circulating digester cooks.

brightnesses are given in Appendix 2.

Figure 11 shows the relation between the Kappa numbers of unbleached pulps and the five stage bleached pulp brightnesses. It reveals that at the same Kappa number, AP can be bleached to higher brightness than FP; and BP (50-50% blended chip pulp) falls approximately halfway between them.

An F*-test was made in order to evaluate the difference of the five stage bleached brightnesses between AP and FP.

The first order term and quadratic term were involved in the regression analysis:

$$F^* = 7.68$$

and

$$6.94 = F\ (0.95;\ 2,\ 4) < F^* = 7.68 < F\ (0.975;\ 2,\ 4) = 10.6$$

Statistical conclusions: For the same Kappa number of unbleached pulp, AP has higher bleaching response (five stage bleaching) than FP at a significance level $\alpha = 0.05$.

Bleaching is known as the second delignification stage following pulping. The results indicate that AP has higher responses to the five stage bleaching, implying that the delignification in AP bleaching is more readily accomplished than in FP. This might be due to the lower molecular weight of lignin in AP.

40 ml CE_1-K Number

In order to follow the course of delignification during the bleaching, the amounts of lignin in the pulps were measured after the CE_1 bleaching stages. Figure 13 indicates that, for the same Kappa number

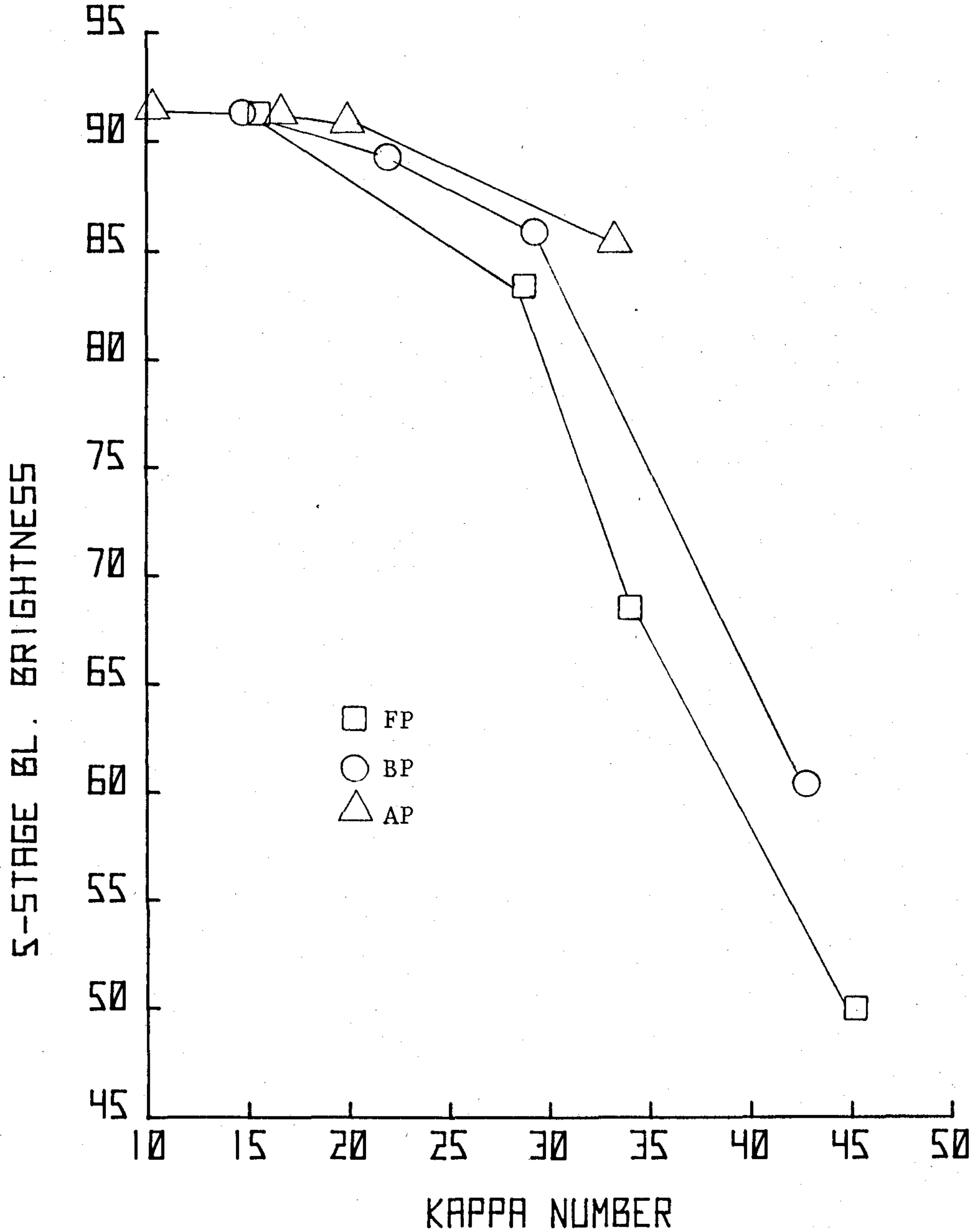

Figure 11. Five-stage bleached pulp brightness vs. Kappa number of unbleached pulp.

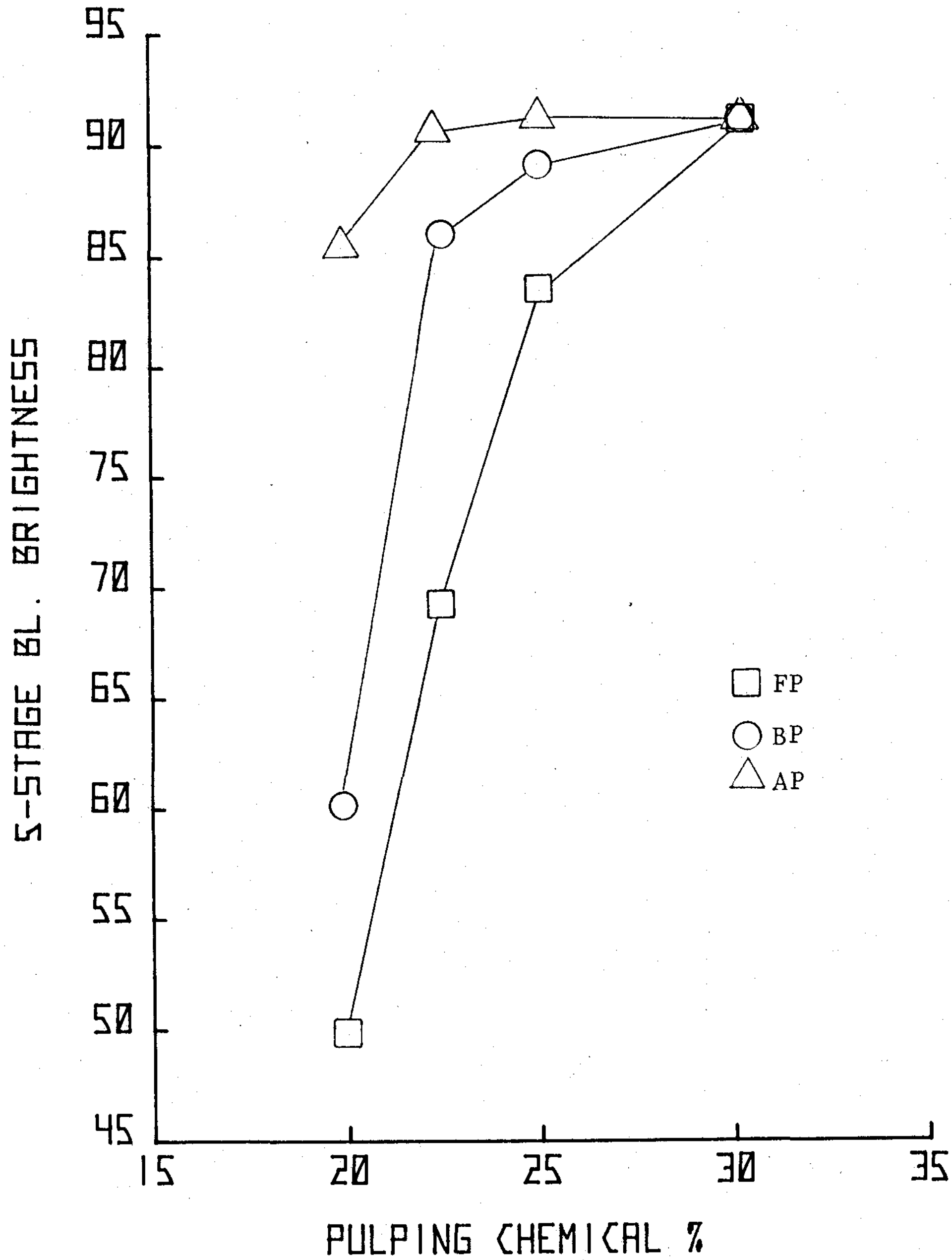

Figure 12. Five-stage bleached brightness vs. pulping chemical charge.

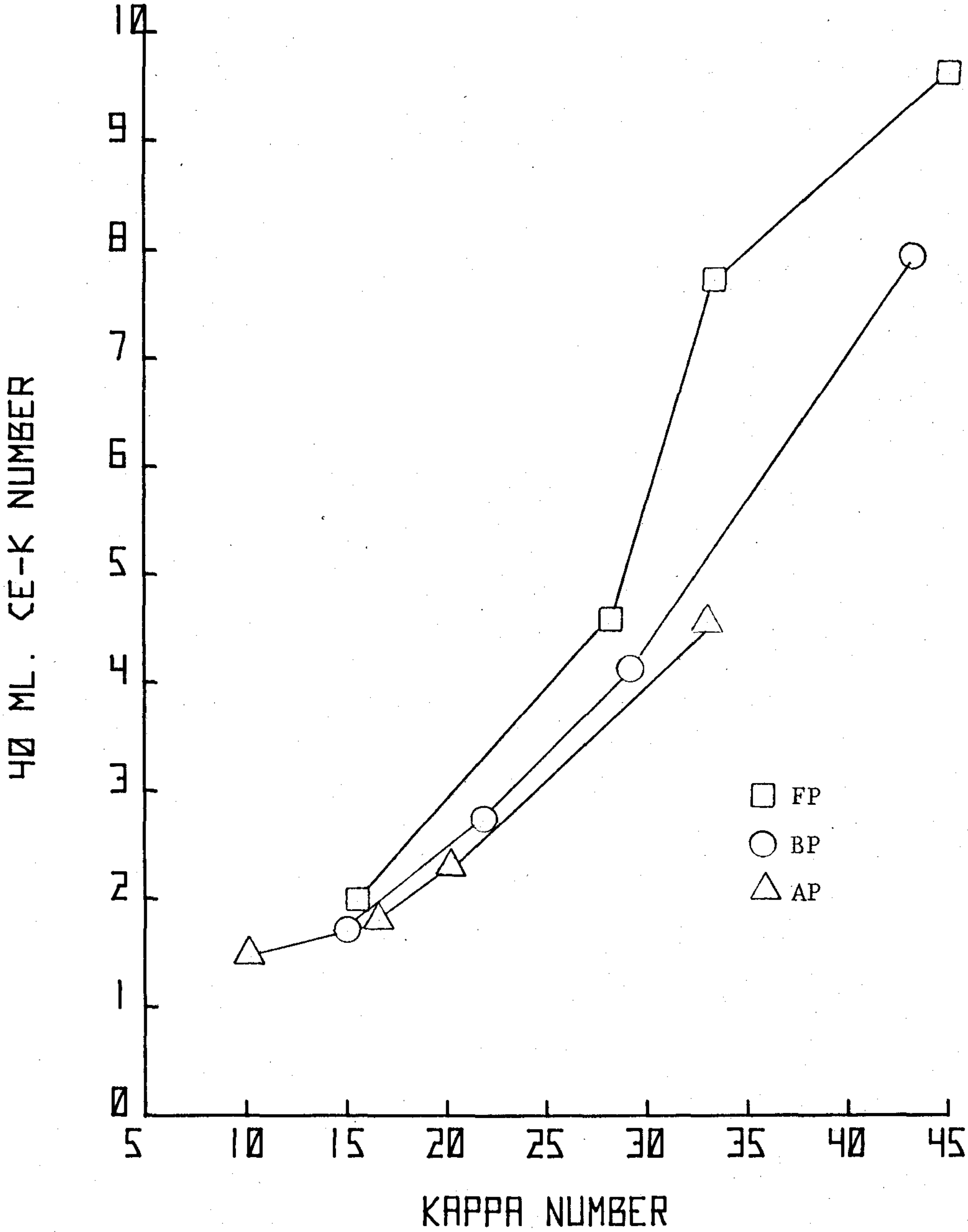

Figure 13. 40 ml. CE_1- K number vs. Kappa number.

of unbleached pulp, AP has a lower CE_1-K number than FP, which means that the residual lignin content in AP is lower than in FP at this point. As previously stated, a degraded wood might have lower molecular weight lignin than a sound wood. Therefore, for the same pulping (first delignification stage) conditions, the former should be pulped to a lower Kappa number. Under the same bleaching (second delignification stage) conditions, the lower molecular weight lignin might be extracted more readily. Figure 12 shows the five stage bleached brightnesses of the 12 circulating digester pulps at four different levels of pulping chemical charge. It shows that the pulps from aged chips have higher bleaching responses than the pulps from fresh chips when all the chemical treatments (pulping and bleaching) were held constant. This implies that the delignification rate in aged chips was more rapid than in fresh chips.

Single Stage Bleached Brightness as a Predictor of Five-Stage Bleached Brightness

Figure 14A and Figure 14B show the relation of five stage bleached pulp brightnesses versus the single stage bleached pulp brightnesses for the exhaustion test and the 30-minute test respectively. Regression models are given in Table 13 and Table 14.

The results show that the five stage bleached brightnesses are strongly correlated with the single stage bleached brightnesses. This means the single stage bleachability test is a good predictor of the five stage bleached brightness, even though the retention time for the single stage bleachability test is limited to 30 minutes.

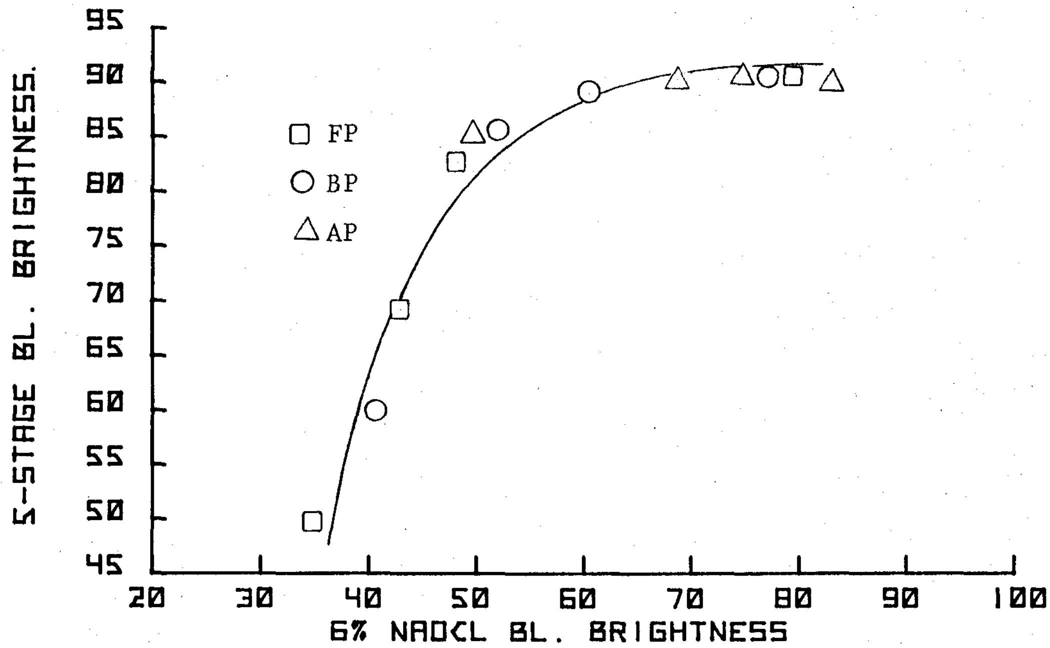

Figure 14A. Five-stage bleached brightness vs. 6% NaOCl bleached brightness (exhaustion test).

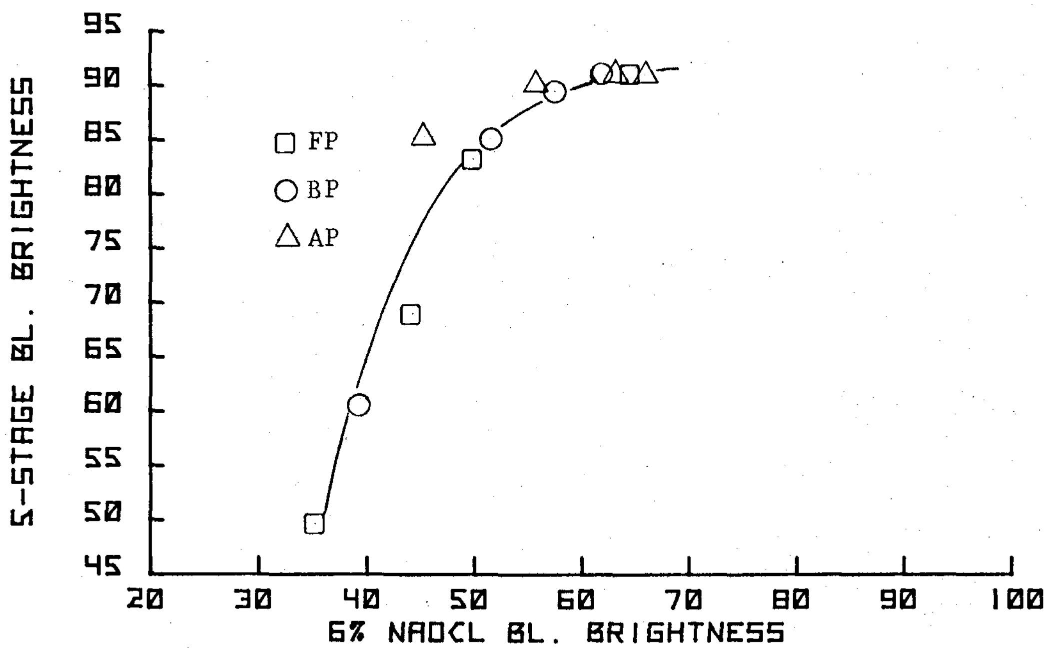

Figure 14B. Five- stage bleached brightness vs. 6% NaOCl bleached brightness (30 minute test).

Table 13. A Regression Model of Five-Stage Bleached Brightness Against Single-Stage Bleached Brightness (Exhaustion Test).

ANOVA $r^2 = 0.97$

Source	DF	SS	MS	F
Regression	1	2165.72	2165.72	306.87
Error	10	70.57	7.06	
Total	11	2236.31		

Term	Coefficient	t*-Value
Constant	92.97	
$e^{-0.10(X)}$	-1641.73	-17.52

X: Single-stage bleached brightness (exhaustion test).

Table 14. A Regression Model of Five-Stage Bleached Brightness Against Single-Stage Bleached Brightness (30-Minute Test).

ANOVA $r^2 = 0.96$

Source	DF	SS	MS	F
Regression	1	2146.16	2146.16	238.11
Error	10	90.13	9.01	
Total	11	2236.33		

Term	Coefficient	t*-Value
Constant	94.18	
$e^{-0.11(X)}$	-2391.93	-15.43

X: Single-stage bleached brightness (30-minute test).

An asymptotic brightness value (about 92) for the CEDED bleaching shown in these two figures implies that there is a maximum brightness level for a certain bleaching sequence. This agrees with the maximum brightness levels of commercial pulps, 91-92.

Viscosity of Pulps

Viscosity is the measure of DP (degree of polymerization) of cellulose in the pulp. Figure 15A shows that at the same Kappa numbers of unbleached pulps, the viscosities of AP are much lower than those of FP. This suggests that the DPs and the pulp strengths of AP are possibly lower. Even though, during the five-stage bleaching treatments, the DP of cellulose is further degraded, the viscosity of the bleached FP retains its superiority over that of the bleached AP. This is shown in Figure 15B.

Figures 16A and 16B show the viscosity of unbleached and bleached pulps at different pulping chemical charges. The cellulose in aged wood and fresh wood were both severely damaged by strong alkali attack (30% pulping chemical charge), resulting in extremely low viscosity pulp.

Application of Kubelka-Munk Theory

The Kubelka-Munk theory (12) of opacity and color reflection is a powerful tool in measuring optical characteristics of paper. Its power lies in the fact that most of the optical phenomena can be explained in terms of two fundamental properties of materials, the scattering coefficient, S, and the absorption coefficient, K. Quite a few practical equations were derived from this basic concept. One of the most

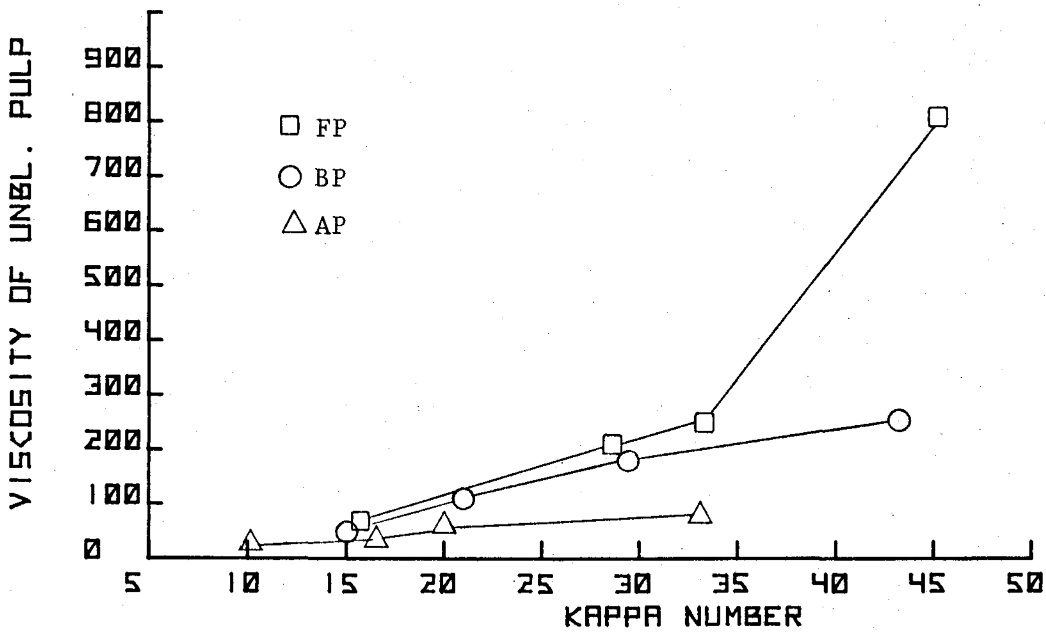

Figure 15A. 1% Cuene viscosity of unbleached pulp vs. Kappa number of unbleached pulp.

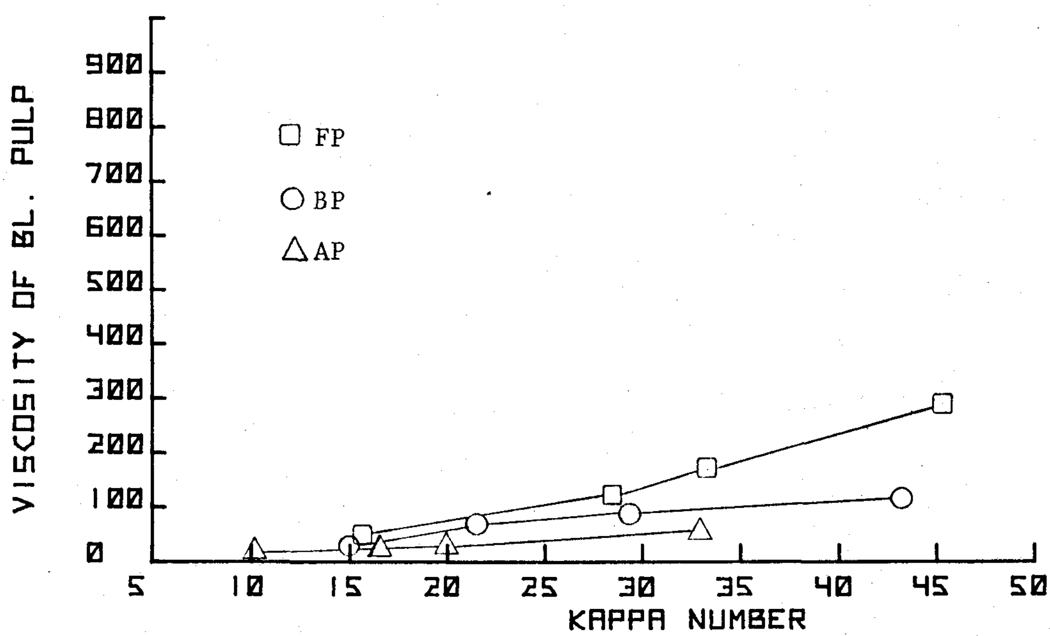

Figure 15B. 1% Cuene viscosity of bleached pulp vs. Kappa number of unbleached pulp.

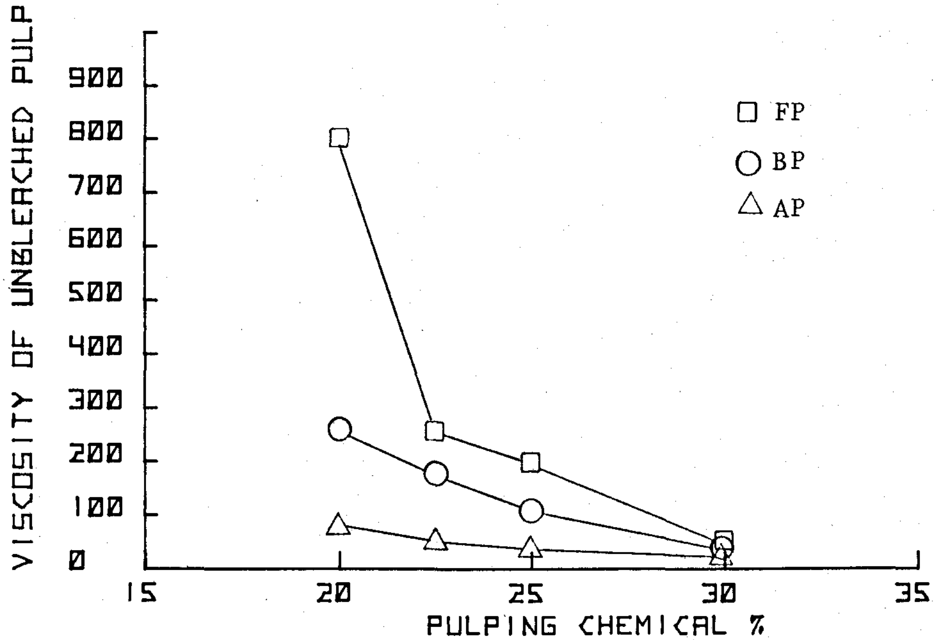

Figure 16A. 1% Cuene viscosity of unbleached pulp vs. pulping chemical charge.

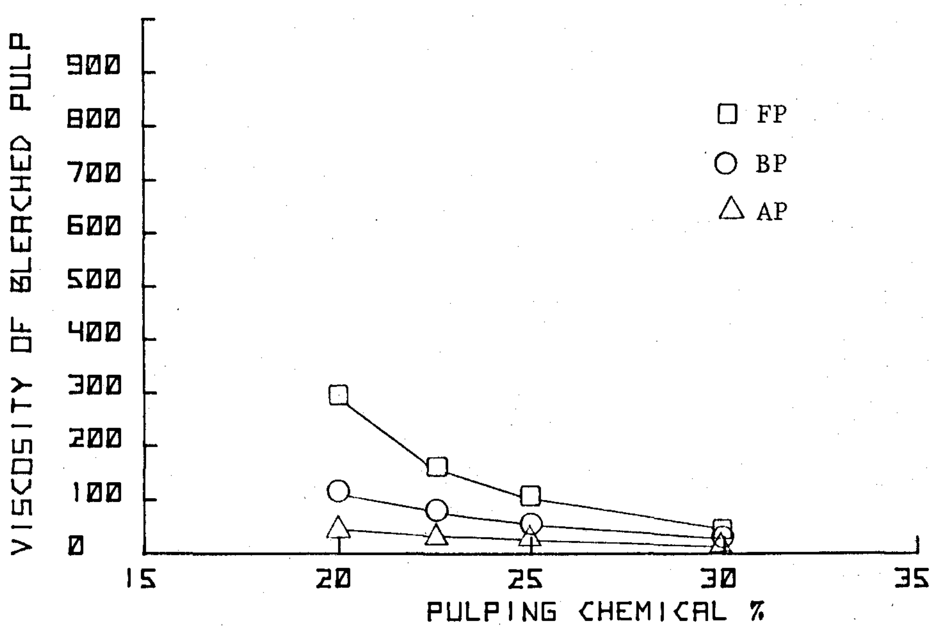

Figure 16B. 1% Cuene viscosity of bleached pulp vs. pulping chemical charge.

useful equations is (13):

$$(R_\infty)_\lambda = 1 + (K/S)_\lambda - [(K/S)_\lambda^2 + 2 \cdot (K/S)_\lambda]^{1/2}$$ or conversely

$$(K/S)_\lambda = [1 - (R_\infty)_\lambda]^2/[2 \cdot (R_\infty)_\lambda]$$

where: $(R_\infty)_\lambda$ is the reflectance of a substance so thick that further increase in thickness fails to change the reflectance, called reflectivity. For measuring brightness of pulp sheets, the wavelength (λ) of light is at 457 nm, i.e., $(R_\infty)_{457}$, and $(K/S)_{457}$.

From the equations described above, the $(K/S)_{457}$ can be calculated from the measurement of the pulp sheet brightness $(R_\infty)_{457}$ by a reflectometer. This kind of expression has been used for the study of color changes in groundwood pulps after aging (14, 15), in the form of "Post Color" number (PC number). This is the difference between the K/S values before (a) and after (b) aging:

$$PC = 100\ [{}^{a}(K/S)_{457} - {}^{b}(K/S)_{457}]$$

In this study, the PC concept was applied to the five stage bleaching instead of to pulp aging (color reversion). Under this circumstance, the PC number is the difference between the K/S values before (a) and after (b) bleaching, or in other words, it implies the "color removal." A higher PC number means higher bleaching response.

The K/S values and PC numbers are given in Appendix 11. The relationship between the PC numbers of five stage bleaching and the Kappa numbers of unbleached pulp is shown in Figure 17. At the same Kappa number, the AP has higher PC number than FP. This means that the color removal in AP is more readily accomplished, i.e., the AP has

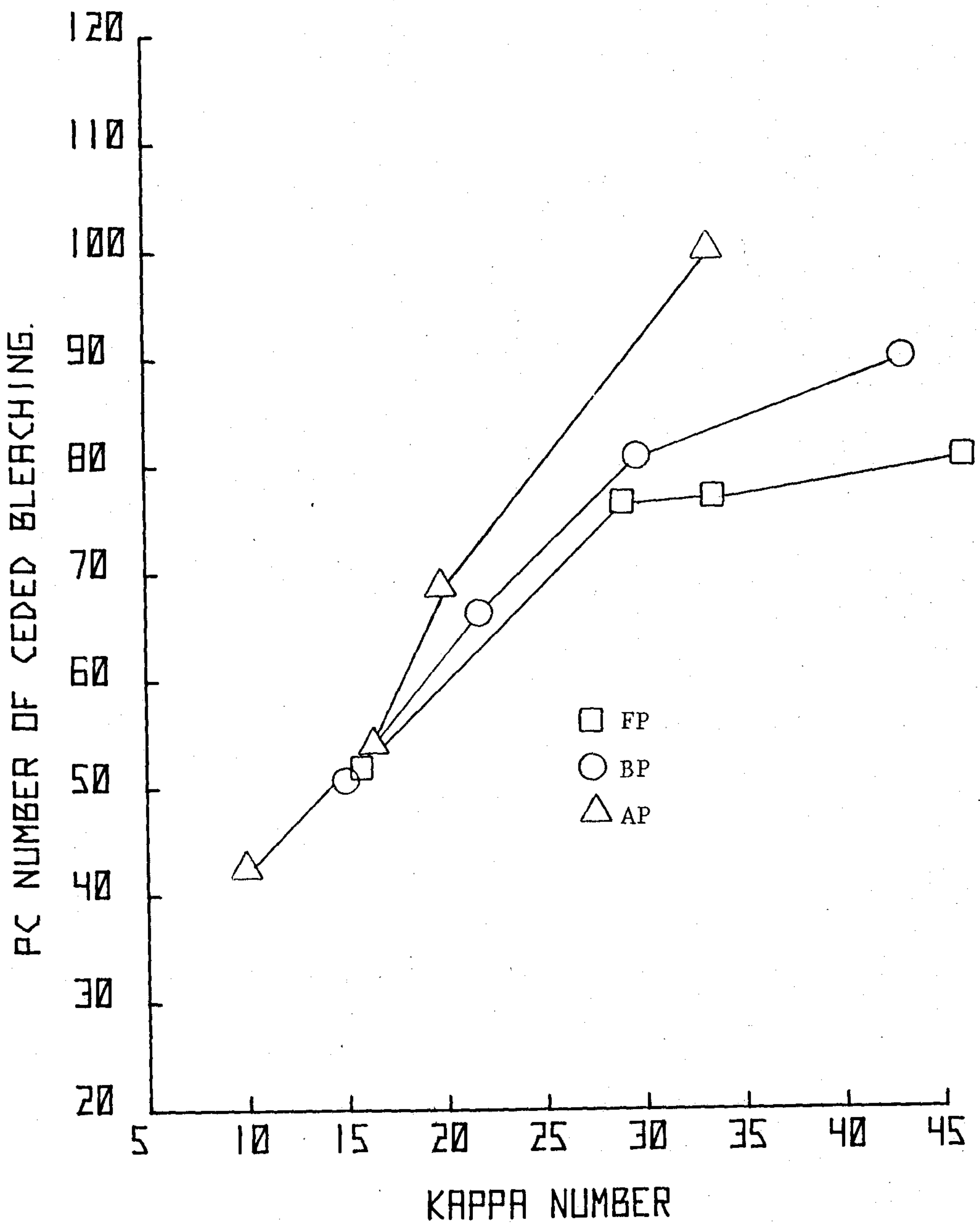

Figure 17. PC number of five-stage (CEDED) bleaching vs. Kappa number of unbleached pulp.

higher bleaching response than FP. However, at low Kappa number (less than 18), there is little difference in bleaching response between AP and FP.

Conclusions

1. The effects of aged chips on the yields, Kappa numbers, and brightnesses of unbleached pulps produced in the circulating digester were similar to the effects observed from the bomb cooks.

2. At the same Kappa number, pulp from aged chips has lower yield and lower unbleached brightness than the pulp from fresh chips.

3. Single stage bleached pulp brightnesses were well correlated with Kappa numbers. However, the difference of bleaching response between AP and FP is not significant.

4. AP is superior to FP in five stage bleaching response, at the same Kappa number.

5. The delignification rate of AP is more rapid than that of FP. This has been confirmed by the results of Kappa number tests following the same pulping conditions and CE_1-K number tests following the equivalent bleaching treatments.

6. The single stage bleaching test appears valid for predicting the final brightness of commercial multi-stage bleaching.

7. A substantial difference of pulp viscosity was found between the AP and FP. However, as the pulping chemical charge increases, the difference decreases. The low viscosity of AP implies that AP may be physically weaker than FP.

8. At the same Kappa number, AP has a higher PC number than FP, implying that the "color-removal" of AP is greater than FP, i.e., AP has higher bleaching response than FP.

Results of Wood Species Identification

The results show that there are about 85 percent Douglas-fir chips in the fresh chips and 90 percent in the aged chips. Those fibers other than Douglas-fir were not identified, but all of them were softwood fibers, and they might be mixtures of hemlock, true fir, etc.

SUMMARY

Utilization of aged wood for pulping is becoming more commonplace in the Pacific Northwest. The effects of aged wood chips on the properties of unbleached kraft pulp are quite well known. However, the bleaching response of the pulps from aged wood chips has not been established. This project investigated the bleachabilities of kraft aged chip pulp (AP) through single-stage bleaching and multi-stage bleaching.

During outdoor storage a combination of microbial action and heating might cause the various components of wood to be degraded into smaller alkali-soluble fragments by chemically changing their structure. Usually, the results of the aging processes should lead to a loss of carbohydrates and a relative gain in lignin. However, the changes in carbohydrates and lignin contents depend on the conditions of degradation and types of microorganisms involved. The chemical structures of lignin and extractives in the chips may have changed as a result of aging, and this may have increased their absorptivity to light. Consequently, an aged wood chip usually is darker than a freshly cut wood chip. More research is suggested in this area.

Wood chips with a lower carbohydrate content and a lower degree of polymerization (DP) should result in a pulp with a lower yield, while a wood chip with lower DP lignin might be pulped to a lower Kappa number. In this study, the effects of commercial Douglas-fir aged chips on the properties of unbleached kraft pulps were investigated under the variables of time, temperature, chemical charge, and sulfidity. It was

found that, when cooking conditions were held constant, AP had lower yield, lower Kappa number, but higher unbleached brightness than FP (pulps from fresh chips). It was also found that the pH's and residual alkali in the waste liquors of AP were lower than those of FP. These results confirmed the hypothesis described previously. At the same Kappa number of unbleached pulp, the unbleached brightnesses of AP were lower than those of FP, but the differences were small. Pulps with the same Kappa number should have nearly the same lignin content. The lower brightness of AP might be due to the higher light-absorbency of the lignin which probably has a different structure from the lignin in the original unaged wood. However, as chemical charge goes higher, the difference between the unbleached brightnesses of AP and FP became indistinguishable.

Single-stage bleached pulp brightnesses were well correlated with Kappa numbers, but the difference in bleaching response between AP and FP is not significant. However, at the same Kappa number of unbleached pulp, AP shows its superior bleachability to FP in five-stage bleaching. The CE_1-K number tests show that, at the same Kappa number of unbleached pulp, the residual lignin contents in AP were lower than those in FP after the second stage bleaching, which means that the lignin in AP can be removed more readily. Therefore, in five-stage bleaching, AP had a higher bleaching response than FP in spite of the inferiority of the former in unbleached pulp brightness.

From the results of the pulping, bleaching, and CE_1-K number tests, a conclusion can be reached that the delignification rates in aged chips and AP were more rapid than those in fresh chips and FP during the pulping and bleaching steps, respectively. This phenomena might be caused by lower molecular weight lignin in the aged chips which occurred as a result of the aging process in the chip pile which were more extractable to alkali. Further research work on this point is recommended.

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APPENDICES

APPENDIX 1
PULPING DATA FOR BOMB COOKS

CODED PARAMETER LEVELS*						RESULTS						
COOK NO.	TIME	TEMP.	CHEM.	SULF.	AGED CHIP	YIELD %	KAPPA NO.	UNBL. BRT.	PH	RESID ALK.	4% BL. NAOCL BRT.	8% BL. NAOCL BRT.
1	3	3	3	3	3	45	39	25.6	12.5	11.7	35.4	51.2
2	3	3	3	3	3	45	40	23.5	12.3	11.5	38.2	49.0
3	3	3	3	3	3	45	40	24.5	12.5	11.6	35.1	49.3
4	3	3	3	3	3	45	36	26.3	12.5	11.5	37.3	53.5
5	3	3	3	3	3	46	40	25.4	12.8	11.9	33.8	47.2
6**	3	3	3	3	3	44	45	24.3	12.8	11.7	33.7	47.2
7	3	3	3	3	3	45	39	26.8	12.8	11.7	35.5	53.8
8	1	3	3	3	3	47	62	22.1	13.0	11.9	28.0	38.7
9	5	3	3	3	3	43	33	27.1	13.0	11.1	38.6	58.5
10	3	5	3	3	3	41	22	28.3	12.8	10.4	50.1	73.0
11	3	1	3	3	3	51	78	20.2	13.0	12.2	23.4	27.8
12	3	3	1	3	3	67	99	11.8	9.7	1.2	9.8	10.8
13	3	3	5	3	3	41	15	33.1	13.3	21.9	62.4	81.0
14	3	3	3	3	1	50	49	22.2	13.0	12.2	28.6	41.4
15	3	3	3	3	5	41	30	25.9	12.8	10.5	41.5	61.7
16	2	2	2	2	4	56	85	15.4	12.2	5.7	17.7	20.3
17	4	2	2	2	2	56	93	15.7	11.3	5.2	18.9	22.8
18	2	4	2	2	2	52	81	17.7	12.3	4.9	19.9	25.6
19	4	4	2	2	4	48	70	18.3	12.5	6.5	23.4	28.5
20	2	2	4	2	2	48	54	24.4	13.2	18.1	29.7	39.2
21	4	2	4	2	4	42	27	29.8	13.1	17.5	40.1	58.0
22	2	4	4	2	4	40	17	32.1	13.1	16.1	53.7	68.7
23	4	4	4	2	2	40	15	31.5	13.1	16.8	55.9	69.7
24	2	2	2	4	2	57	89	16.6	12.4	7.2	16.3	18.8
25	4	2	2	4	4	49	78	17.6	11.4	6.7	20.3	24.5
26	2	4	2	4	4	47	71	17.1	11.2	6.2	22.4	27.3
27	4	4	2	4	2	50	68	17.5	11.6	6.8	22.2	26.7
28	2	2	4	4	4	43	31	28.4	13.1	17.8	39.4	54.2
29	4	2	4	4	2	46	28	28.6	13.2	18.1	41.4	54.5
30	2	4	4	4	2	43	18	31.2	13.1	17.5	60.1	79.6
31	4	4	4	4	4	38	14	31.9	13.1	16.2	67.8	84.3
32	3	3	3	1	3	46	52	24.4	12.9	11.1	29.8	39.6
33	3	3	3	5	3	43	25	28.3	13.0	15.9	46.2	69.3

* For actual cooking conditions, refer to Table 1 in text.

** An extra control cook was added, making a total of 33.

APPENDIX 2

Pulping Data of Circulating Digester Cooks

	Variables		Results							
							6% NaOCl bleached brightness		Five-stage bleaching	
Cook number	Chemical charge* %	Aged chip %	Unscreened Yield %	Screened Yield %	Kappa number	Unbleached brightness	Exhaustion** test	30 minute test	40 ml CE_1-K number	Bleached brightness
1	20	0	49.7	47.6	45.7	25.7	35.8	36.4	9.6	49.7
2	20	50	46.6	43.6	42.9	26.3	41.0	38.1	8.0	60.2
3	20	100	40.0	37.0	32.9	26.5	50.0	46.4	4.6	85.6
4	22.5	0	47.0	46.7	33.3	29.4	43.1	44.0	7.8	68.5
5	22.5	50	42.6	42.3	28.7	30.1	52.7	51.8	4.2	86.2
6	22.5	100	38.4	38.2	20.0	32.9	68.1	56.7	2.4	91.0
7	25	0	45.4	45.2	28.2	30.6	48.6	49.4	4.6	83.3
8	25	50	41.8	41.6	21.9	33.2	60.9	56.8	2.7	89.0
9	25	100	37.5	37.4	17.0	36.9	75.3	62.8	1.8	91.7
10	30	0	42.7	42.7	16.1	37.6	78.8	64.4	2.0	91.7
11	30	50	40.2	40.2	15.1	37.8	76.1	62.2	1.7	91.7
12	30	100	36.3	36.3	10.2	40.8	83.3	64.7	1.5	91.6

Sulfidity = 20%
Temperature = 170°C
Time to temperature = 45 minutes

Time at temperature = 120 minutes
Liquor:wood ratio = 7.5:1
Capacity = 900 grams of o.d. chips for each cook

*Chemical charge is based on o.d. weight of chips.

**Retention time ends at the exhaustion of NaOCl, which can be examined by using Starch-KI indicator.

APPENDIX 3

Viscosity of Digester Pulps

Cook number	Kappa number	Viscosity of unbleached pulp*	Viscosity of bleached pulp
1	45.7	803	294
2	42.9	261	113
3	32.9	82	58
4	33.3	261	173
5	28.7	185	89
6	20.0	58	31
7	28.2	201	109
8	21.9	110	61
9	17.0	41	26
10	16.1	69	45
11	15.1	65	40
12	10.2	28	19

*TAPPI T 230 su-66. Unbleached pulp was treated with sodium chlorite before dissolving in cupriethylenediamine solvent.

APPENDIX 4

Twenty Multiple Regression Variables

The 20 variables include 5 first-order terms, 5 square terms, and 10 cross-product terms, listed as follows:

Variable number	Subject
1	(Time)
2	(Temperature)
3	(Chemical)
4	(Sulfidity)
5	(Chip Ratio)
6	$(\text{Time})^2$
7	(Time) · (Temperature)
8	(Time) · (Chemical)
9	(Time) · (Sulfidity)
10	(Time) · (Chip Ratio)
11	$(\text{Temperature})^2$
12	(Temperature) · (Chemical)
13	(Temperature) · (Sulfidity)
14	(Temperature) · (Chip Ratio)
15	$(\text{Chemical})^2$
16	(Chemical) · (Sulfidity)
17	(Chemical) · (Chip Ratio)
18	$(\text{Sulfidity})^2$
19	(Sulfidity) · (Chip Ratio)
20	$(\text{Chip Ratio})^2$

APPENDIX 5

STATISTICAL T-DIRECTED SEARCH PROCEDURE

PULP YIELD

```
F-REG:  31.4; F-RED:   0.0; R-SQ:  0.98; C-P:   19.00

        T =              0.50
VAR'S OUT:  4  6  8 10 17 20   VAR'S IN:  1  2  3  5  7  9 11 12 13 14 15 16 18 19
F-REG:  65.0; F-RED:   0.1; R-SQ:  0.98; C-P:    7.43

        T =              1.00
VAR'S OUT:  5  9 11 12   VAR'S IN:  1  2  3  7 13 14 15 16 18 19
F-REG:  96.7; F-RED:   0.2; R-SQ:  0.98; C-P:    1.25

        T =              1.50
VAR'S OUT:  7 13 14 18   VAR'S IN:  1  2  3 15 16 19
F-REG: 158.8; F-RED:   0.4; R-SQ:  0.97; C-P:   -4.00

        T =              2.00
VAR'S OUT:
        T =              2.50
VAR'S OUT:
        T =              3.00
VAR'S OUT:
  ****************************************************************
```

Variables 1 to 20, see Appendix 4.

APPENDIX 6

STATISTICAL T-DIRECTED SEARCH PROCEDURE

KAPPA NUMBER

F-REG: 18.1; F-RED: 0.0; R-SQ: 0.97; C-P: 19.00

T = 0.50
VAR'S OUT: 7 9 16 17 18 20 VAR'S IN: 1 2 3 4 5 6 8 10 11 12 13 14 15 19
F-REG: 36.7; F-RED: 0.1; R-SQ: 0.97; C-P: 7.65

T = 1.00
VAR'S OUT: 8 10 12 13 VAR'S IN: 1 2 3 4 5 6 11 14 15 19
F-REG: 54.0; F-RED: 0.3; R-SQ: 0.96; C-P: 1.64

T = 1.50
VAR'S OUT: 14 19 VAR'S IN: 1 2 3 4 5 6 11 15
F-REG: 62.1; F-RED: 0.4; R-SQ: 0.95; C-P: 0.24

T = 2.00
VAR'S OUT:

T = 2.50
VAR'S OUT: 6 VAR'S IN: 1 2 3 4 5 11 15
F-REG: 60.2; F-RED: 0.7; R-SQ: 0.94; C-P: 1.95

T = 3.00
VAR'S OUT: 4 5 11 VAR'S IN: 1 2 3 15
F-REG: 58.8; F-RED: 1.7; R-SQ: 0.89; C-P: 14.76

****

Variables 1 to 20, see Appendix 4.

APPENDIX 7

STATISTICAL T-DIRECTED SEARCH PROCEDURE

UNBLEACHED PULP BRIGHTNESS

F-REG: 22.9; F-RED: 0.0; R-SQ: 0.97; C-P: 19.00

T = 0.50

VAR'S OUT: 10 16 VAR'S IN: 1 2 3 4 5 6 7 8 9 11 12 13 14 15 17 18 19 20

F-REG: 29.6; F-RED: 0.0; R-SQ: 0.97; C-P: 15.05

T = 1.00

VAR'S OUT: 8 9 14 18 19 VAR'S IN: 1 2 3 4 5 6 7 11 12 13 15 17 20

F-REG: 46.4; F-RED: 0.3; R-SQ: 0.97; C-P: 7.35

T = 1.50

VAR'S OUT: 5 6 7 17 VAR'S IN: 1 2 3 4 11 12 13 15 20

F-REG: 54.7; F-RED: 0.8; R-SQ: 0.96; C-P: 5.98

T = 2.00

VAR'S OUT: 2 4 11 12 13 20 VAR'S IN: 1 3 15

F-REG: 67.5; F-RED: 2.8; R-SQ: 0.87; C-P: 31.90

T = 2.50

VAR'S OUT: 1 15 VAR'S IN: 3

F-REG: 167.5; F-RED: 3.2; R-SQ: 0.84; C-P: 42.48

T = 3.00

VAR'S OUT:

****

Variables 1 to 20, see Appendix 4.

APPENDIX 8

STATISTICAL T-DIRECTED SEARCH PROCEDURE

RESIDUAL ALKALI

```
F-REG:  77.8; F-RED:   0.0; R-SQ:  0.99; C-P:   19.00

        T =              0.50
VAR'S OUT:  1  4 13 14 15   VAR'S IN:  2  3  5  6  7  8  9 10 11 12 16 17 18 19 20
F-REG: 141.8; F-RED:   0.1; R-SQ:  0.99; C-P:    9.43

        T =              1.00
VAR'S OUT:  2  6  8 20   VAR'S IN:  3  5  7  9 10 11 12 16 17 18 19
F-REG: 199.8; F-RED:   0.3; R-SQ:  0.99; C-P:    3.84

        T =              1.50
VAR'S OUT: 10 11   VAR'S IN:  3  5  7  9 12 16 17 18 19
F-REG: 260.3; F-RED:   0.3; R-SQ:  0.99; C-P:    0.24

        T =              2.00
VAR'S OUT:  7 16 17 19   VAR'S IN:  3  5  9 12 18
F-REG: 284.8; F-RED:   1.1; R-SQ:  0.98; C-P:    6.16

        T =              2.50
VAR'S OUT:  5  9   VAR'S IN:  3 12 18
F-REG: 453.5; F-RED:   1.2; R-SQ:  0.98; C-P:    5.72

        T =              3.00
VAR'S OUT: 12   VAR'S IN:  3 18
F-REG: 550.0; F-RED:   1.6; R-SQ:  0.97; C-P:   12.61
```

****

Variables 1 to 20, see Appendix 4.