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Comparisons were made between anthraquinone modified soda pulp (soda-AQ), and methanol modified kraft (kraft-MeOH) and sulfite (sulfite-MeOH) pulps on western Oregon Douglas-fir. The kappa number, yield, brightness, and deshive values were all measured. The soda-AQ and kraft-MeOH pulps were the traditional brown color but the sulfite-MeOH pulps came out of the digester a bright yellow which darkened on exposure to ultraviolet light. The sulfite-MeOH pulps deshived at the highest yield of the three at 65% yield. The percent heartwood was varied in each case and had very little effect on the soda-AQ and kraft-MeOH pulps. It did cause a 45 point increase in kappa number in the sulfite-MeOH pulps. In both the kraft-MeOH and sulfite-MeOH pulps the chips pulped the fastest with 30% methanol in the liquor. Strength tests on the kraft-MeOH pulps showed strengths equivalent to those of traditional kraft cooks but the sulfite-MeOH strength values were considerably lower than those of the traditional kraft cooks.

Alternative Methods for Production of Douglas-fir Linerboard Quality Pulp

by

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ALTERNATIVE METHODS FOR PRODUCTION OF DOUGLAS-FIR LINERBOARD QUALITY PULP

INTRODUCTION

Almost all linerboard produced today is made by the kraft pulping process. Kraft pulping has its disadvantages in that yields are low, the pulp is dark, and the reduced sulfur compounds released into the atmosphere are effluvial. On the other hand, the process is cost effective and the pulp is very strong. This is needed for the production of linerboard quality pulp.

If a method could be found to eliminate some of the problems associated with traditional kraft pulping, the industry should be interested. This constitutes the focal point of this thesis.

The objectives of this thesis were first, to study three types of pulping processes for kappa-yield relationships, brightness, and deshive values, and secondly to study the strength properties of any pulps that looked promising from the first set of experiments. The three types of pulping processes studied were:

1. Soda-anthraquinone pulping.
2. Kraft-methanol pulping.
3. Sulfite-methanol pulping.

The kraft-methanol and sulfite-methanol pulps were chosen for strength testing due to the results from the first set of experiments.

LITERATURE REVIEW

Linerboard production is one of the mainstays of the U.S. kraft industry, accounting for 14.558 million tons in 1981.[1] Kraft pulping, however, results in low pulp yields and emits reduced sulfur compounds, which are extremely odoriferous, into the atmosphere.

Kraft pulping technology was first introduced in 1879[3] and by the 1920's the basic technology was well established. In the 1930's G.H. Tomlinson in Canada pioneered work on modern recovery boilers.[6] This development caused the basic kraft technology to become firmly established. The only major improvements since then have been in equipment.[2]

The kraft industry has several advantages and disadvantages according to Lowe.[2] The advantages are:

1. Proven economics and technology.
2. Excellent pulp strengths.
3. Can pulp any species.
4. Applicable for producing many grades.
5. Good fuel economy.

The disadvantages are:

1. A complex, technical process.
2. High capital investment costs.
3. High costs of air and water pollution control.
4. Low pulp yields which results in high pulpwood requirements.

The other major full chemical pulp produced today is by the sulfite process. The first sulfite pulp mill started production in

1874 under the auspices of C.D. Ekman in Sweden.[6] Sulfite pulp was used almost exclusively where a light colored pulp was needed until the 1930's when it was learned how to bleach kraft pulp with no serious losses in strength. Kraft pulps have often been the pulps of choice because of their better paper strength properties.[3] Two major factors had made the sulfite industry less competitive than the kraft industry. These factors were:[3]

1. Sensitivity to the wood raw material.
2. Difficulty in recovering the cooking chemicals and utilization of the waste products.

The introduction of soluble bases and their recovery as well as the recovery of sulfur dioxide[6] has greatly lessened the impact of (2) above but (1) is still a major problem in the sulfite industry.

Douglas-fir (Pseudotsuga menziesii) can easily be pulped by the kraft process but cannot easily be pulped by the acid sulfite process[3,4,5] because of the presence of the phenolic extractive dihydroquercetin. This extractive tends to reduce bisulfite to thiosulfate, resulting in decreased stability of the cooking acid.[3] This in turn leads to high screenings and a high lignin content of the accepted pulp. The pulp comes out of the digester a bright yellow[4] which is thought to be due to the oxidation of dihydroquercetin to quercetin.[3]

Worster[7] has suggested that the following criteria will have to be met for any process to challenge the dominance of kraft pulping. The proposed process must:

1. Be free of inorganic sulfides capable of forming reduced sulfur compounds.

2. Avoid use of strong acids or alkalis to prevent degradation of cellulose and hemicelluloses.
3. Be capable of solubilizing lignin without attacking cellulose and hemicelluloses or modifying lignin so that it can contribute to the desired end products.
4. Use a simpler recovery process than kraft that does not cause environmental problems.
5. Not use multiple stages, significantly higher pressures or longer cooking times than current chemical pulping processes. These factors might raise the capital investment costs.

Several modifications of the kraft process have been examined recently in an attempt to increase the yield of the kraft process. These modifications have included H_2S pretreatment of the chips which can result in a yield increase of 4.5 to 7%[2], depending on the species.[8] The technology for this process is marketed by MacMillan Bloedel Ltd.

A second type of modification to the system is the polysulfide process. Variations on this theme are offered by Union Camp Corporation and the Mead Corporation. This type of process would be relatively inexpensive to adapt to an existing kraft mill but the polysulfide liquor does tend to increase corrosion problems.[2]

The use of additives during pulping can also help to increase yields. The additive that has received the most attention recently is anthraquinone because it seems to be the most effective delignification catalyst yet discovered.[9] Anthraquinone is, however, relatively expensive and so usage is feasible only when wood costs are high, when wood is difficult to pulp,[10] or when the mill is capacity limited by the digesters or by the recovery boiler.

Mill trials have been made with a kraft-anthraquinone system on Southern pine chips to produce a linerboard quality pulp. The benefits were as great or greater than those observed in the lab. The most probable cause of this would be build-up of anthraquinone levels in the black liquor. Recycling of the black liquor would then lead to higher than applied charges of anthraquinone which means less anthraquinone may be needed to obtain a given effect than lab studies indicate.[22]

Anthraquinone is not a true catalyst because it is only partially recoverable after pulping. According to Fullerton et at.[11] the most likely reason for anthraquinone's effectiveness as a pulping catalyst is related to its ability, in the reduced anthrahydroquinone form, to undergo condensation reactions with the lignin derived quinone methides. This may also be why anthraquinone is only partially recoverable after pulping.

According to Basta and Samuelson[12] the addition of anthraquinone to Scandanavian spruce led to a marked increase in the delignification rate and slower dissolution of the carbohydrates. They also found that anthraquinone catalyzed delignification during the entire cook and that pulp viscosity was significantly improved by the presence of anthraquinone.

Löwendahl and Samuelson[13] state that the addition of anthraquinone in soda pulping leads to oxidation of the reducing end groups of cellulose and the hemicelluloses to form aldonic acid end groups which are comparatively stable to the alkaline peeling reaction. Therefore, the increase in pulp yield at a given lignin content may be a combination of the catalyzed delignification and the oxidized stabilization of the reducing end groups of the carbohydrates.

Work by Kosíková et. al.[14] suggests that the presence of anthraquinone in soda cooking liquor stabilizes the components of the residual pulp against acid and alkaline treatment and that the anthraquinone-anthrahydroquinone system induces reductive cleavage of the structural elements of lignin which might otherwise give rise to carbonyl groups.

Another alternative which has been given attention through the years is pulping by the use of solvents. Klason first discovered, in 1893, that ethyl alcohol in conjunction with a small amount of hydrochloric acid will dissolve part of the lignin matrix.[15] Later work showed that a combination of solvent and water worked better than solvent alone and that the use of hydrochloric acid as a catalyst was not necessary if temperatures of 175-185°C were used.[16]

Recently a considerable amount of work has been done on the use of organic solvents such as methanol[21] and ethanol[17] in aqueous-alcohol pulping systems. Both alcohols have been intensively studied recently and have had laboratory successes but at this time neither has been commercially successful.

Methanol, at this time, is being studied in conjunction with both acid and alkaline cooking systems. Nakano et. al.[18] and Daima et. al.[19,20] have determined the following results from the use of alkali (NaOH) - methanol cooking:

1. Delignification by alkali-methanol cooking is[18] faster than by kraft cooking.

2. Comparing at the same lignin content, there is no[18] difference in sheet strengths except for the tear factor which is lower for solvent pulps.

3. The rapid delignification during cooking is due to[18,19] the prevention of condensation through the methylation of active benzyl alcohol groups in the lignin molecule.

4. The alkaline peeling reaction is suppressed due to[18,20] the slower isomerization of an end group and/or the formation of metasaccharinic acid.

Methanol has also been used with acid sulfite systems to accelerate delignification. Bublitz and Hull[21] have developed a process to produce a high yield, fully defibered western hemlock (Tsuga heterophylla) pulp in one hour or less. The following results were determined:

1. The wood was fully defibered in one hour at 165-170°C with yields of 60-65%.

2. The pulp strengths appear to be equivalent to those of commercial sulfite pulps.

3. For western hemlock the solvent ratio exhibited an optimum at 30% methanol - 70% water w/w and the liquor exhibited an optimum at 70% free - 30% combined SO_2 based on total SO_2.

Solvent pulping with methanol appears to hold promise of high yields and fast cooking times but would require a completely new and fully enclosed mill to implement this system. At this time no feasible recovery process for the solvent has been outlined.

EXPERIMENTAL PROCEDURES

Statistical Model

This experimental pulping plan was set up using "a central composite rotatable second order design (Cochran and Cox)[23] with five processing variables".[21] The central conditions were chosen as optimal from preliminary experimentation. Three sets of 32 cooks each were made by varying the five parameters of each series as listed in Tables 1, 2, and 3. Parameter C indicates the ratio of sapwood to heartwood, with one-hundred minus the percent heartwood giving the percent sapwood. Therefore, when the percent heartwood is listed as zero, the percent sapwood is 100 percent. The percent NaOH as Na_2O and the percent anthraquinone are given as percent on oven dry wood. The percent methanol is given as percent of the liquor including the water in the chips. The percent free SO_2 is the percent free SO_2 of the total SO_2 in the liquor. In each case the cooks were brought up to temperature in 45 minutes.

Table 4 details how the parameters listed in Tables 1, 2, and 3 were combined in each of the 32 cooks per series.

The raw data was entered into a multiple regression program designed for the Hewlett-Packard 9825A Desk Top Calculator. A "best" reduced model was calculated for each of the tests made on the pulp. The independent variables of the multiple regression listed on Table 5 are the five levels (M.R. Variables 1-5), their squares (M.R. Variables 6, 11, 15, 18, 20), and their ten cross products.

TABLE 1 : Soda-Anthraquinone pulping parameters.

		Level				
Parameter	Variable	1	2	3	4	5
A	Temperature °C	150	160	170	180	190
B	Time (at temp.)	30	45	60	75	90
C	% Heartwood	0	25	50	75	100
D	% NaOH as Na_2O	14.0	18.2	22.4	26.6	30.8
E	% Anthraquinone	0	.04	.08	.12	.16

TABLE 2 : Kraft-Methanol pulping parameters.

		Level				
Parameter	Variable	1	2	3	4	5
A	Temperature °C	150	160	170	180	190
B	Time (at temp.)	0	7.5	15	22.5	30
C	% Heartwood	0	25	50	75	100
D	% Methanol	0	15	30	45	60
E	% Anthraquinone	0	.04	.08	.12	.16

TABLE 3 : Sulfite-Methanol pulping parameters.

		Level				
Parameter	Variable	1	2	3	4	5
A	Temperature °C	150	160	170	180	190
B	Time (at temp.)	15	30	45	60	75
C	% Heartwood	0	25	50	75	100
D	% Methanol	0	15	30	45	60
E	% Free SO_2	50	60	70	80	90

All cooks brought to temperature in 45 minutes
Kraft-Methanol cooks made with 22.4% AA and 25% sulfidity
Sulfite-Methanol cooks made with 20% total SO_2 on o.d. wood

TABLE 4 : Parameter levels for the 32 cook series of pulping experiments.

	Parameter Level				
Cook Number	A	B	C	D	E
1	3	3	3	3	3
2	3	3	3	3	3
3	3	3	3	3	3
4	3	3	3	3	3
5	3	3	3	3	3
6	3	3	3	3	3
7	1	3	3	3	3
8	5	3	3	3	3
9	3	1	3	3	3
10	3	5	3	3	3
11	3	3	1	3	3
12	3	3	5	3	3
13	3	3	3	1	3
14	3	3	3	5	3
15	3	3	3	3	1
16	3	3	3	3	5
17	2	2	2	2	4
18	2	2	2	4	2
19	2	2	4	2	2
20	2	2	4	4	4
21	2	4	2	2	2
22	2	4	2	4	4
23	2	4	4	2	4
24	2	4	4	4	2
25	4	2	2	2	2
26	4	2	2	4	4
27	4	2	4	2	4
28	4	2	4	4	2
29	4	4	2	2	4
30	4	4	2	4	2
31	4	4	4	2	2
32	4	4	4	4	4

TABLE 5 : List of the multiple regression variables.

Multiple Regression Variable Number	Process Variable	
1	0 x 1	Temperature, °C
2	0 x 2	Time (min. at temperature)
3	0 x 3	% Heartwood
4	0 x 4	% NaOH (Soda-AQ) % Methanol (Kraft-MeOH) % Methanol (Sulfite-MeOH)
5	0 x 5	% Anthraquinone (Soda-AQ) % Anthraquinone (Kraft-MeOH) % Free SO_2 (Sulfite-MeOH)
6	1 x 1	
7	1 x 2	
8	1 x 3	
9	1 x 4	
10	1 x 5	
11	2 x 2	
12	2 x 3	
13	2 x 4	
14	2 x 5	
15	3 x 3	
16	3 x 4	
17	3 x 5	
18	4 x 4	
19	4 x 5	
20	5 x 5	

Looking at Cook 16 for example, which has parameters A through D at level 3 and parameter E at level 5, the values to be entered into the multiple regression equations are as follows:

Multiple Regression Variable Number	Parameter	Level	Value Entered into M.R. Equations
1	A	3	3
2	B	3	3
3	C	3	3
4	D	3	3
5	E	5	5
6	A x A	3 x 3	9
7	A x B	3 x 3	9
8	A x C	3 x 3	9
9	A x D	3 x 3	9
10	A x E	3 x 5	15
11	B x B	3 x 3	9
12	B x C	3 x 3	9
13	B x D	3 x 3	9
14	B x E	3 x 5	15
15	C x C	3 x 3	9
16	C x D	3 x 3	9
17	C x E	3 x 5	15
18	D x D	3 x 3	9
19	D x E	3 x 5	15
20	E x E	5 x 5	25

The "best" reduced model was found by the technique of t-directed search in which the initial model contained all the potential independent variables. Those independent variables which did not meet a predetermined t-value were sequentially eliminated from the initial model, leaving reduced models.

The "best" set of independent variables was then determined by the reduced model in which the C_p value was the smallest. The C_p value is the standardized total squared error of the n fitted observations for the regression model. It contains both a bias component and a random error component. The C_p value is calculated by:

$$C_p = \frac{SSE_p}{\hat{\sigma}^2} - (n - 2p)$$

Where: SSE_p = Sums of Squares Error with p parameters

$\hat{\sigma}^2$ = unbiased estimator of the true error variance

n = number of observations

p = number of parameters in the regression equation

Confidence bounds on the transformed linear regression lines for Figures 13 - 15 were calculated by the Working and Hotelling[24] method. This method is used for regressions of the form $E(Y) = \beta_o + \beta_1 X$. At any level X_h the bounds are given by:

$$\hat{Y}_h - Ws(\hat{Y}_h) \leq \beta_o + \beta_1 X_h \leq \hat{Y}_h + Ws(\hat{Y}_h)$$

Where: $W^2 = 2F(1 - \alpha;\ 2,\ n-2)$

$Y_h = b_o + b_1 X_h$

$$s^2(\hat{Y}_h) = MSE \left[\frac{1}{n} + \frac{(X_h - \overline{X})^2}{\Sigma(X_i - \overline{X})^2} \right]$$

$$MSE = \frac{\Sigma(Y_i - Y_i)^2}{n - 2}$$

Wood Source

In this series of experiments, wood samples were obtained from the butt ends of one or more Douglas-fir logs cut from McDonald Forest which is located six miles northwest of Corvallis, Oregon on Highway 99W. The samples contained approximately equal parts of sapwood and heartwood. The samples were split, the bark removed, and the heartwood and sapwood separated by color. The pieces were then chipped, hammermilled, and allowed to air dry. Once the chips were air dried they were screened on a Williams round hole screen and the oversized fraction was removed. For the tube cooks, only the -3/8, +3/16 inch fraction was used due to the small diameter of the tubes. The circulating liquor digester was able to handle all remaining chip sizes.

Pulping Equipment

The first series of pulping experiments was made in tube digesters composed of a piece of 316 stainless steel pipe one foot long and one inch in diameter, welded closed at one end and fitted with a quarter turn ball valve at the other end. These tubes held 15 grams of chips (oven dry basis) at a 7:1 liquor to wood ratio including the water in the chips. The digesters were heated ten at a time in a thermostatically controlled oil bath of Polyglycol E-1500 which was oscillated 30 times per minute for liquor circulation.

The second series of pulping experiments was made in a stainless steel circulating liquor digester with a basket capacity of one kilogram oven dry chips and a 7:1 liquor to wood ratio including the water in the chips. The liquor was circulated via an external pump and the digester was heated with electric band heaters.

Liquor Make-up

Stock solutions of NaOH and Na_2S were made up in the laboratory from the chemicals and distilled water.

The soda liquor was made up by mixing NaOH stock solution and distilled water to the required active alkali concentration.

The kraft liquor was made up by mixing up Na_2S and NaOH stock solutions together with distilled water to the required active alkali concentration and percent sulfidity.

The sodium based sulfite liquor was made up first by mixing Na_2SO_3 pellets and water to form a solution of sodium sulfite. An H_2SO_3 solution was made by bubbling SO_2 gas through cold water until saturated. These two solutions were mixed together by weight and titrated immediately prior to use.

Pulp Processing and Testing

The tube cooks were removed from the oil bath at the required time and immediately immersed in cold water. Once the digesters had cooled they were opened and a liquor sample taken. The contents of the digester were then rinsed into a one liter Waring blender and beat on high speed until the cooked portions of the chips were defibrated. The pulp was then poured into a Buchner funnel lined with

Whatman No. 1 filter paper, rinsed twice with distilled water, and air dried. The pads were then weighed and moisture content samples taken. The bulk of the pads were then stored in plastic bags. Brightness and CIE colors were measured on the Elrepho Colorimeter according to TAPPI* (Technical Association of the Pulp and Paper Industry) Standards T217 m-48[25] and T216 m-47.[26] Kappa numbers were measured according to TAPPI Standard T236 m-60.[27] Deshive values were assigned by a procedure in which the pulps receive a value from zero to ten. A value of ten indicates a fully defibered pulp (no shives) and a zero indicates no defibration.

The circulating liquor digester cooks had the liquor blown at the required time and the chips were then removed from the basket and allowed to cool. They were then weighed and moisture content samples taken. The chips were beaten in the PFI mill to four different freenesses according to TAPPI Standards T248 pm-74[28] and T277 m-58.[29] Handsheets were then made according to TAPPI Standard T205 os-71,[30] conditioned according to TAPPI Standard T402 os-70,[31] and tested according to TAPPI Standards T217 m-48[25] and T220 os-71.[32] Kappa numbers were done according to TAPPI Standard T236 m-60.[27]

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* For information on TAPPI Standards, write to Standards Administrator, Technical Association of the Pulp and Paper Industry, One Dunwoody Park, Atlanta, Georgia 30341

RESULTS AND DISCUSSION

Soda -Anthraquinone Cooks

Results from the soda-AQ cooks indicate low yields, the central conditions (level 3) giving a total yield of 50% at a kappa number of 63. The brightness was 26% at the central conditions, increasing for longer times or higher temperatures and decreasing for shorter times or lower temperatures. The "best" reduced models of the regression equations for kappa, yield, and deshive value are found in Appendix 2.

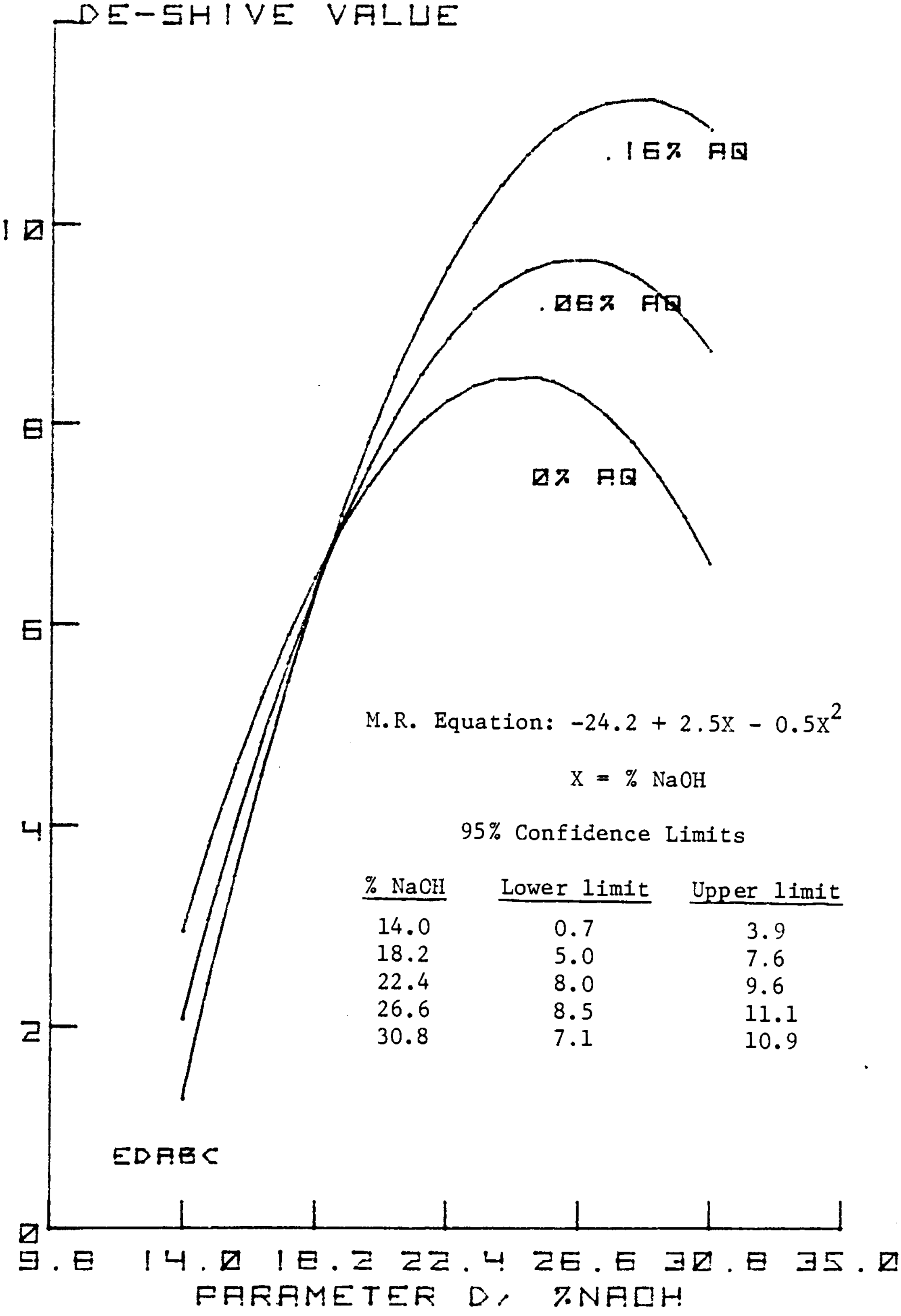
The beta coefficients (numerical coefficients) of the full regression models were stored on tape for the HP-9835A Desk Top Calculator and were used to draw Figures 1 through 11. These figures all illustrate calculated regression lines, not actual, measured values.

Figures 1 through 3 illustrate some of the results of these soda-AQ cooks.

Figure 1 shows a graph of the percent NaOH vs. deshive value while covarying the percent anthraquinone. The 95% confidence limits on the .08% AQ regression line indicate that there is no significant difference in deshive value at the .16% AQ level but there may be a significant difference at the 0% AQ level at the higher amounts of NaOH in the system.

Figure 2 shows the percent NaOH vs. total yield while covarying the percent heartwood. It is interesting to note that, at 20% NaOH, the yield is almost the same for the 100% sapwood, 50-50

FIGURE 1 : Soda-Anthraquinone pulp data illustrating % NaOH vs. Deshive value with covariation of the % AQ



M.R. Equation: $-24.2 + 2.5X - 0.5X^2$

X = % NaOH

95% Confidence Limits

% NaCH	Lower limit	Upper limit
14.0	0.7	3.9
18.2	5.0	7.6
22.4	8.0	9.6
26.6	8.5	11.1
30.8	7.1	10.9

FIGURE 2 : Soda-Anthraquinone pulp data illustrating % NaOH vs. Total yield with covariation of the % Heartwood

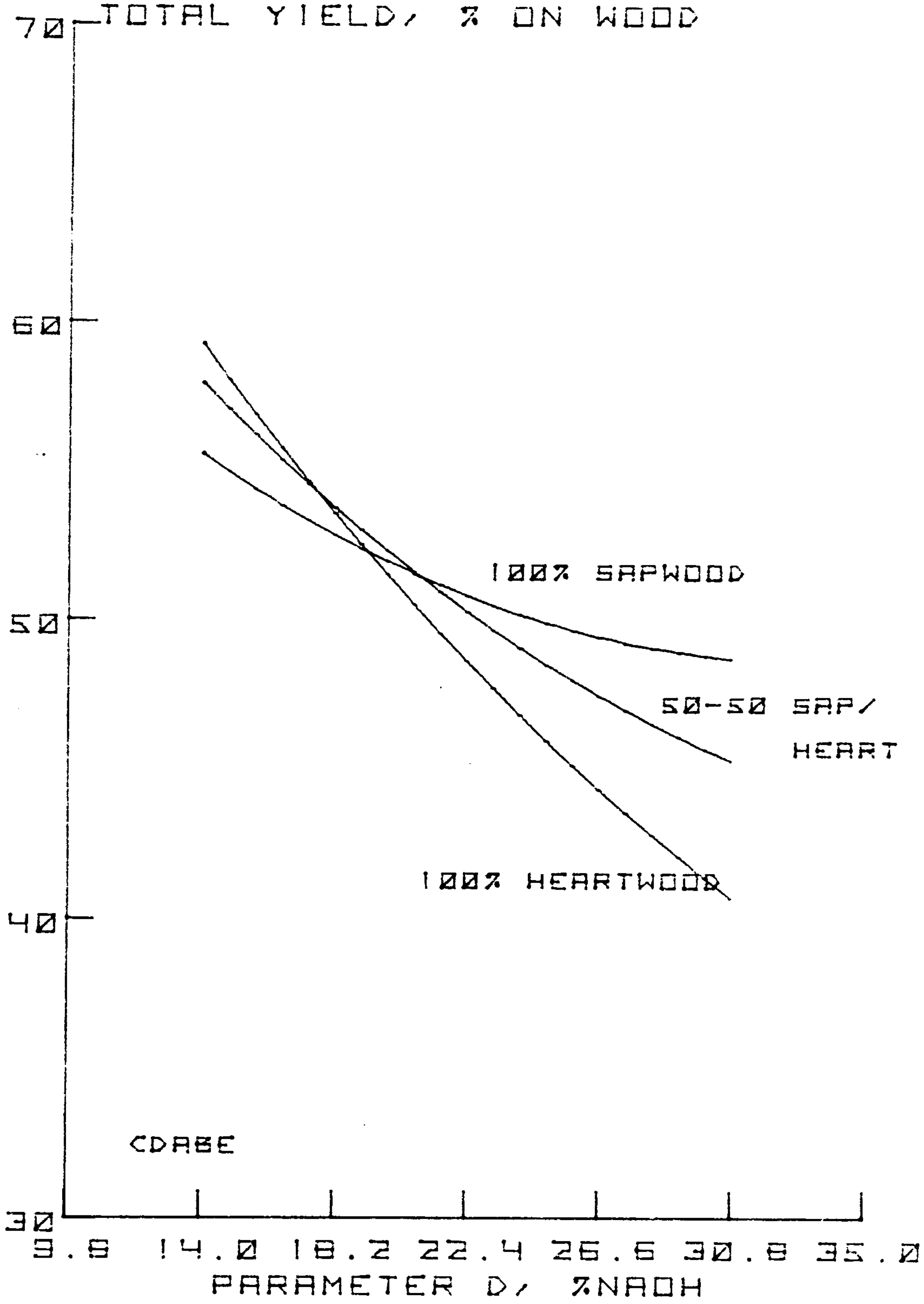
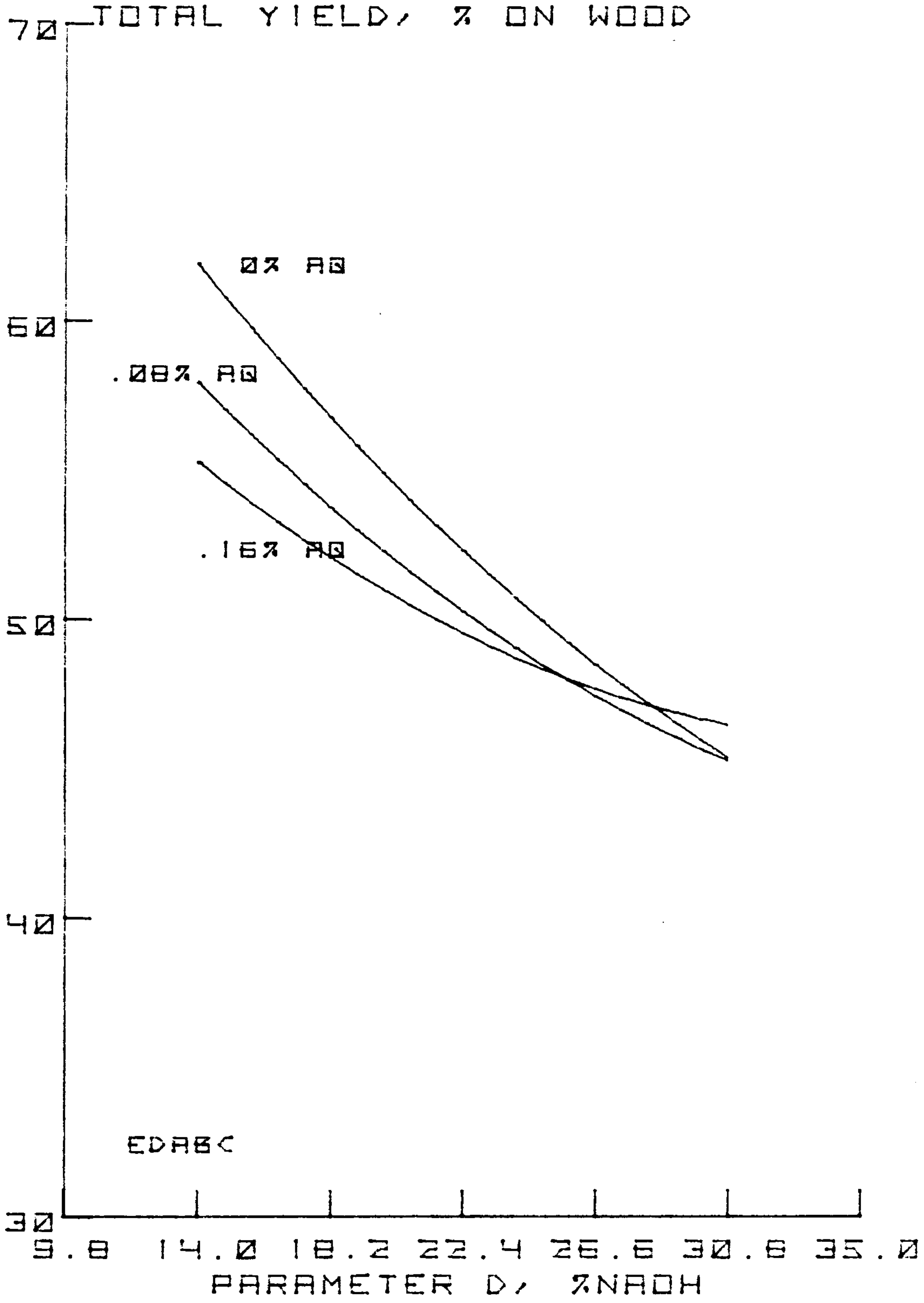


FIGURE 3 : Soda-Anthraquinone pulp data illustrating % NaOH vs. Total yield with covariation of the % AQ



mixture of sap- and heartwood, and the 100% heartwood. The difference at the central conditions of 22.4% NaOH show only a 2% difference in yield. The difference becomes more pronounced only at the higher concentrations of NaOH.

Figure 3 shows that just the opposite relationship holds true for the percent NaOH vs. total yield while covarying the percent anthraquinone. The difference in yield is the most pronounced at the minimum percent NaOH of 14%. The yield is the lowest for the most anthraquinone, indicating faster pulping, whereas no significant difference in yield is seen at levels 4 and 5 of NaOH.

Kraft-Methanol Cooks

The kraft-MeOH cooks show a better kappa-yield relationship than the soda-AQ cooks. In this situation, at the central conditions the yield is 55% and the kappa number is 81. The cooks were well deshived at the central conditions with a deshive value of 8.5 out of a maximum of 10. The brightnesses were comparable to those of traditional kraft cooks. The "best" reduced models of the regression equations for kappa, yield, and deshive values are found in Appendix 2.

Figures 4 through 7 illustrate some of the results of the kraft-MeOH cooks.

Figure 4 illustrates percent methanol vs. kappa number with covariation of the cooking temperature. This indicates that a minimum in kappa number is reached at just over 30% methanol in the liquor, suggesting that the pulping rate is the fastest at the 30% solvent level. As can be seen from the graph, a 20°C change in temperature makes a large difference in the pulping rate. This, of course, is to be expected from current pulping theory.

Figure 5 illustrates temperature vs. total yield with co-variation of the percent anthraquinone. As would be expected, the yield drops sharply with increasing temperature. The anthraquinone level, however, appears to have a minimal effect on the pulping rate. The greatest effect is observed at the lowest temperature. At higher temperatures the pulping rate accelerates as the theory of the H-factor states, minimizing the effects of the anthraquinone. Note that at a temperature of 170°C there is no difference between the yields of cooks having no anthraquinone and those having .08% anthraquinone.

Figure 6 shows total yield vs. deshive value while covarying two parameters, in this case the percent methanol and the percent heartwood. On this graph the three separate lines show levels 1, 3, and 5 of methanol in the system (0, 30, and 60%) while the lines themselves start at level 1 of the percent heartwood (0% heartwood $\equiv$ 100% sapwood) and progress to level 5 (100% heartwood $\equiv$ 0% sapwood). This graph indicates that, with no methanol in the liquor, the deshive value is the lowest and the total yield is the highest. The 60% methanol level has lower yield and a better deshive value than the water based cook. However, the 30% methanol level shows a slightly lower yield than the 60% methanol level, but a considerably better deshive value. This shows, therefore, that at the same conditions, the 30% methanol level pulps the fastest of all the levels tested. All three lines fall basically on the same regression line which shows that the amount of methanol present in the system has no effect on the deshive value. Only the total yield affects the deshive value. The regression lines themselves, in each case, start at 100% sapwood, reach a minimum, and then continue on to the 100% heartwood level. The 100% heartwood level in each regression line gives the highest deshive value and the lowest yield. This may be due to removal of the large amount of extractives present in Douglas-fir heartwood by the cooking liquor.

The last figure in this series, Figure 7, shows the kappa number vs. total yield while covarying the percent heartwood and the percent anthraquinone. The individual lines indicate levels of heartwood and along their length move from zero percent anthraquinone to .16% anthraquinone based on oven dry wood. As is indicated in this graph, the amount of anthraquinone present in the cooks has at the most a 2% effect on the yield. As the level of heartwood increases from zero to 100% there is less and less of a change in kappa number concurrent with a change in yield. The amount of anthraquinone added shows the greatest effect on the kappa-yield relationship with 100% sapwood. The 100% sapwood level shows the largest variation with a 1.5% decrease in yield and a drop of 15 points in kappa number. The 50-50 mixture of sapwood and heartwood shows a 1% drop in yield and a 10 point drop in kappa number. The 100% heartwood level shows a 1% decrease in yield with virtually no effect on the kappa number.

FIGURE 4 : Kraft-Methanol pulp data illustrating % MeOH vs. Kappa number with covariation of the pulping temperature

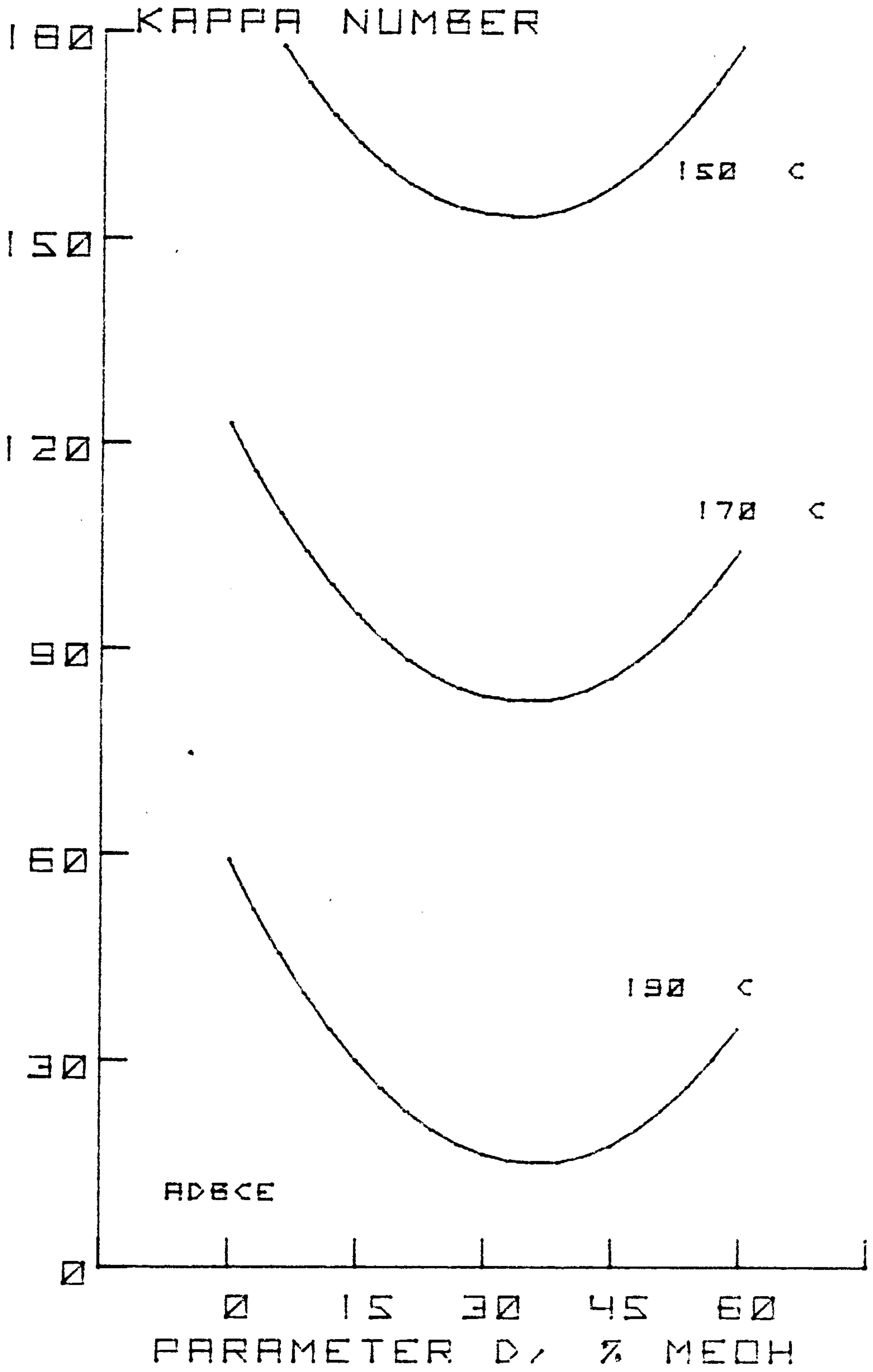


FIGURE 5 : Kraft-Methanol pulp data illustrating Pulping temperature vs. Total yield with covariation of the % AQ

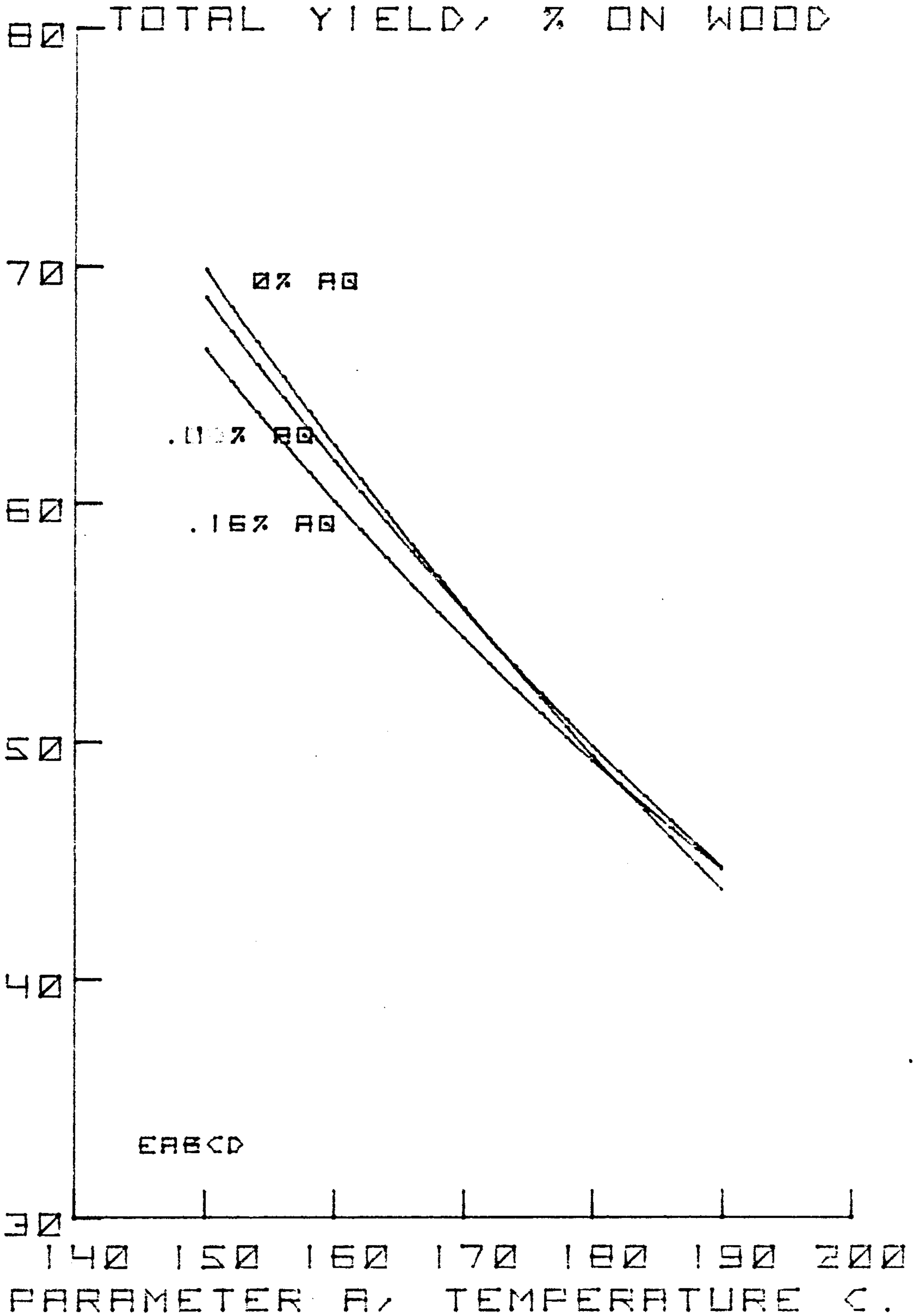


FIGURE 6 : Kraft-Methanol pulp data illustrating Total yield vs. Deshive value with covariation of the % MeOH and the % Heartwood

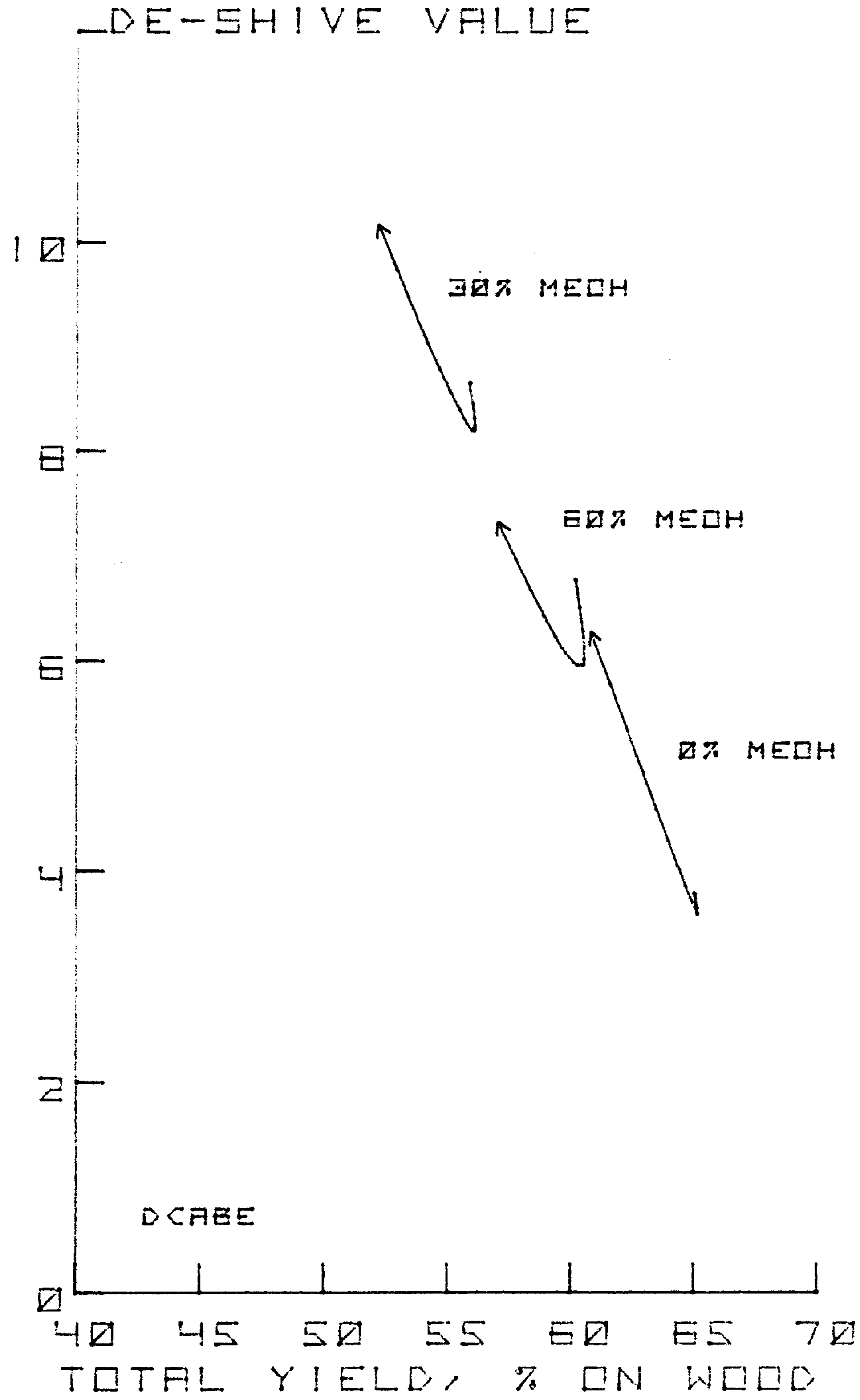
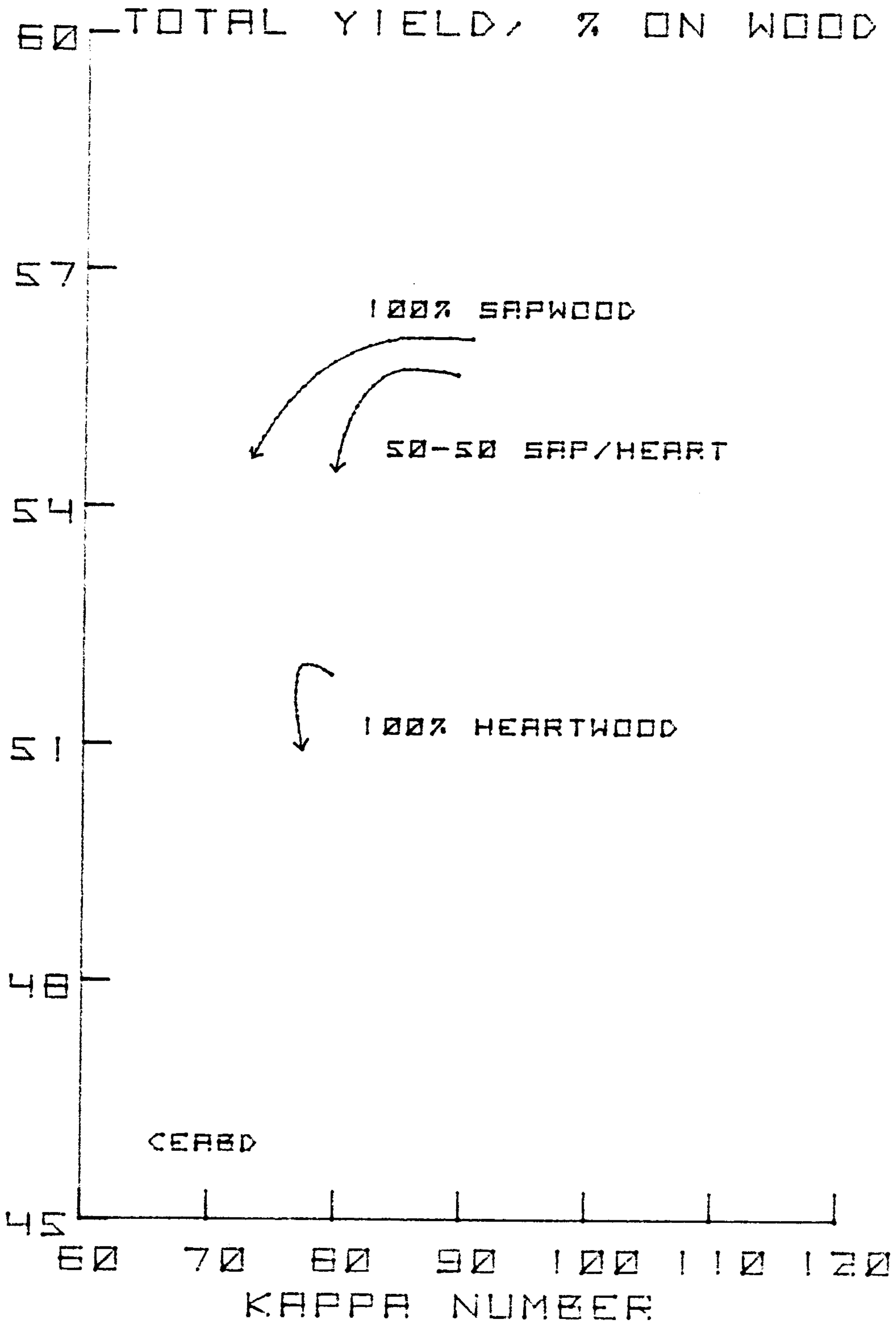


FIGURE 7 : Kraft-Methanol pulp data illustrating Kappa number vs. Total yield with covariation of the % Heartwood and the % AQ



Sulfite-Methanol Cooks

The sulfite-MeOH cooks show a kappa number of 107 and a yield of 63% at the central conditions. The deshive values are also very good with a value of 9 out of 10 maximum. The pulps came out of the digester a bright yellow which is most likely due to the oxidation of dihydroquercetin to quercetin. When the pulps first came out of the digester the brightnesses ranged from 31 to 51, though on exposure to ultraviolet light some of them dropped over 20 points in brightness.

An experiment was made to determine if exposure to ultraviolet light would indeed darken the handsheets made. Four sulfite-MeOH pulps were chosen and two handsheets were made from each one. The pulps chosen had been made the month before, and so had been exposed to ultraviolet light from the sun. One of the handsheets made was stored between two sheets of black paper in a desk drawer and the other was placed under a long wave ultraviolet light for 24 hours. After 24 hours each of the handsheets was measured on the Elrepho Colorimeter on filters 8,[25] 9, 10, and 11.[26] The dominant wavelength and purity of the color was also calculated for each one.

As can be seen from Table 6, even though the pulps had been exposed to ultraviolet light previously, a 24 hour exposure under a concentrated ultraviolet light still darkened the color of the pulp. The change shows up the best in filters 9 and 10 when going from the one month old pulp to that same pulp exposed to ultraviolet light for 24 hours.

TABLE 6 : Brightness and CIE dominant wavelength and color purity for some Douglas-fir sulfite-methanol pulps.

Sulfite Cook No.	8	9	10	11	λ max	Purity
3-orig.	43.7	69.9	64.9	42.1	576	25
3	19.9	54.4	48.5	18.8	576	49
3-UV	19.9	49.2	42.8	19.0	578	44
11-orig.	50.7	73.0	69.0	49.0	576	20
11	27.4	60.1	54.9	26.0	575	40
11-UV	26.2	53.6	47.3	25.2	578	36
12-orig.	36.6	60.2	57.2	35.1	574	27
12	23.4	56.0	50.4	22.3	576	44
12-UV	22.5	51.2	45.2	21.3	577	41
16-orig.	48.5	68.2	62.8	47.5	580	17
16	31.0	61.3	55.3	28.6	577	37
16-UV	29.0	56.3	50.0	28.3	578	33

Regression equations were also calculated for the sulfite-MeOH pulps. The "best" reduced models of the regression equations for kappa, yield, and deshive value are found in Appendix 2.

Figures 8 through 11 illustrate some of the results of the sulfite-MeOH cooks.

Figure 8 illustrates the percent heartwood vs. total yield while covarying the percent free SO_2 (Parameter E). It shows a high yield at 50% free SO_2, indicating a slower pulping time than in the 70 or 90% free SO_2 cooks. This agrees with earlier work by Bublitz and Hull.[21] The regression line at level 3, 70% free SO_2, shows the flattest line of the three, indicating little difference in yield between 100% sapwood and 100% heartwood, all other factors being held constant.

Figure 9 shows the percent heartwood vs. total yield while covarying the percent methanol. This graph is very interesting, showing that at zero percent methanol (a water base cook) the yield decreases drastically as Douglas-fir heartwood is added to the system. Just the opposite relationship holds true for the 60% methanol level. The yield increases with increasing amounts of Douglas-fir heartwood, indicating slower pulping. It is possible that the methanol may help prevent lignin condensation during the acid cooks.[33] The 30% methanol level shows little difference in yield from 100% sapwood to 100% heartwood chips, resulting in a more stable yield at the central conditions. This indicates that the 30% methanol level results in a modified sulfite process that is not nearly so sensitive to the type of wood as a traditional water based acid sulfite cook.

Figure 10 shows kappa number vs. percent yield with covariation of two parameters, the percent methanol and the percent heartwood. The individual lines show the three levels of methanol in the system, and each line starts at zero percent methanol and rises to 60% methanol (levels 1 through 5). Level 1 (0% MeOH) shows a large decrease in yield over a 30 point range in kappa number when going from 100% sapwood to 100% heartwood. Just the opposite relationship again holds for level 5 (60% methanol). The yield increases rapidly as the percent heartwood increases. Level 3, containing 30% methanol, shows only a small change in yield and kappa number going from 100% sapwood to 100% heartwood. This again shows that the 30% methanol level shows the smallest variations in yield.

The same type of relationships hold for Figure 11 as for Figure 10. It shows total yield vs. deshive value with covariation of the percent methanol and the percent heartwood. Again, the individual lines show levels 1, 3, and 5 of the percent methanol with each line ranging from 100% sapwood to 100% heartwood. Level 1 (0% methanol) shows a zero deshive with 100% sapwood and a 6 deshive with 100% heartwood. The level 5 (60% methanol) line shows just the opposite, a deshive of 6 at 100% sapwood and a deshive of zero at 100% heartwood. The level 3 line shows very little difference in deshive value between 100% sapwood and 100% heartwood. This again indicates that the 30% methanol system is much more stable in yield and deshive value to the type of wood than either the zero methanol or 60% MeOH systems.

FIGURE 8 : Sulfite-Methanol pulp data illustrating % Heartwood vs. Total yield with covariation of the % Free SO_2

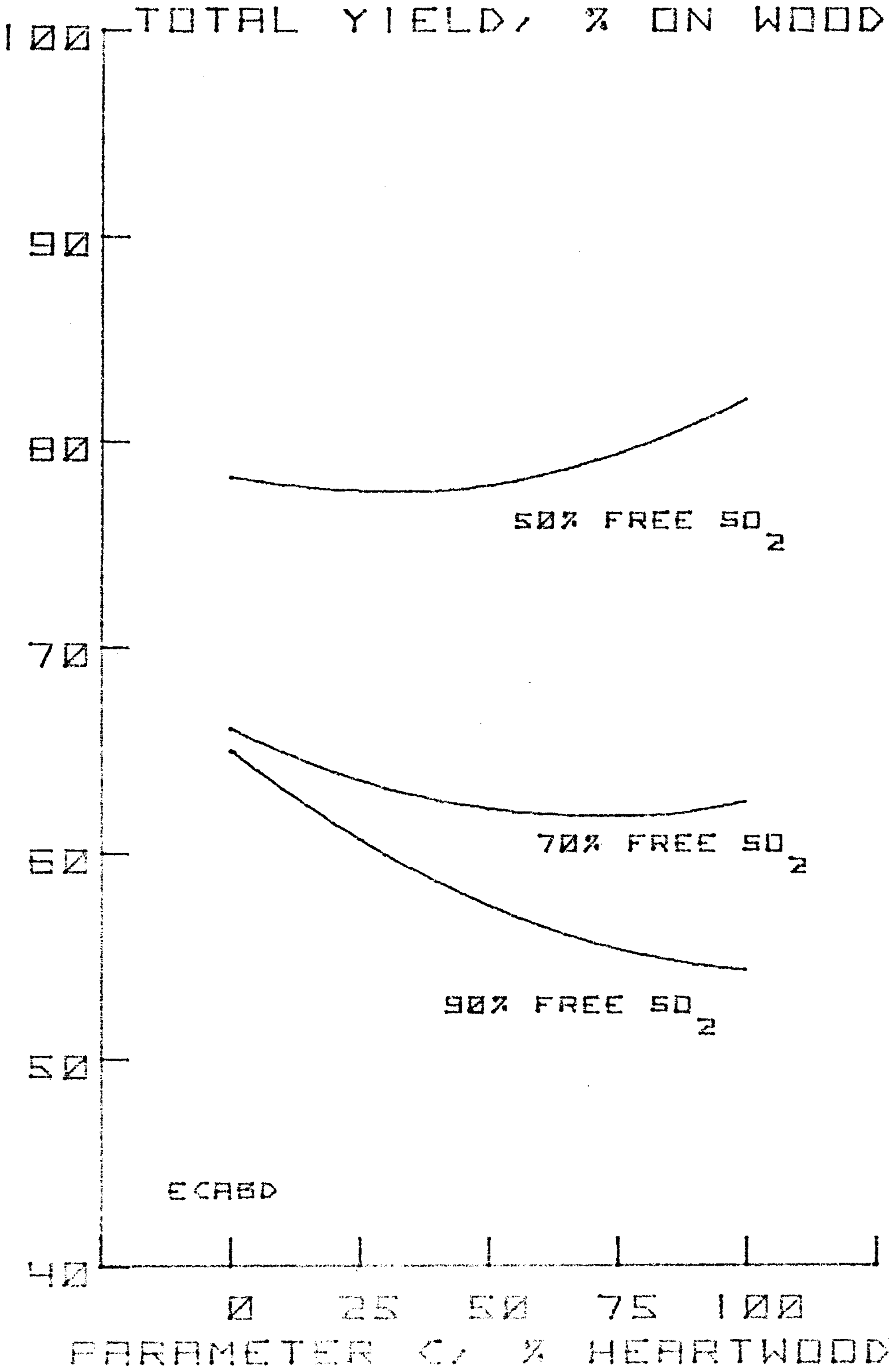


FIGURE 9 : Sulfite-Methanol pulp data illustrating % Heartwood vs. Total yield with covariation of the % MeOH

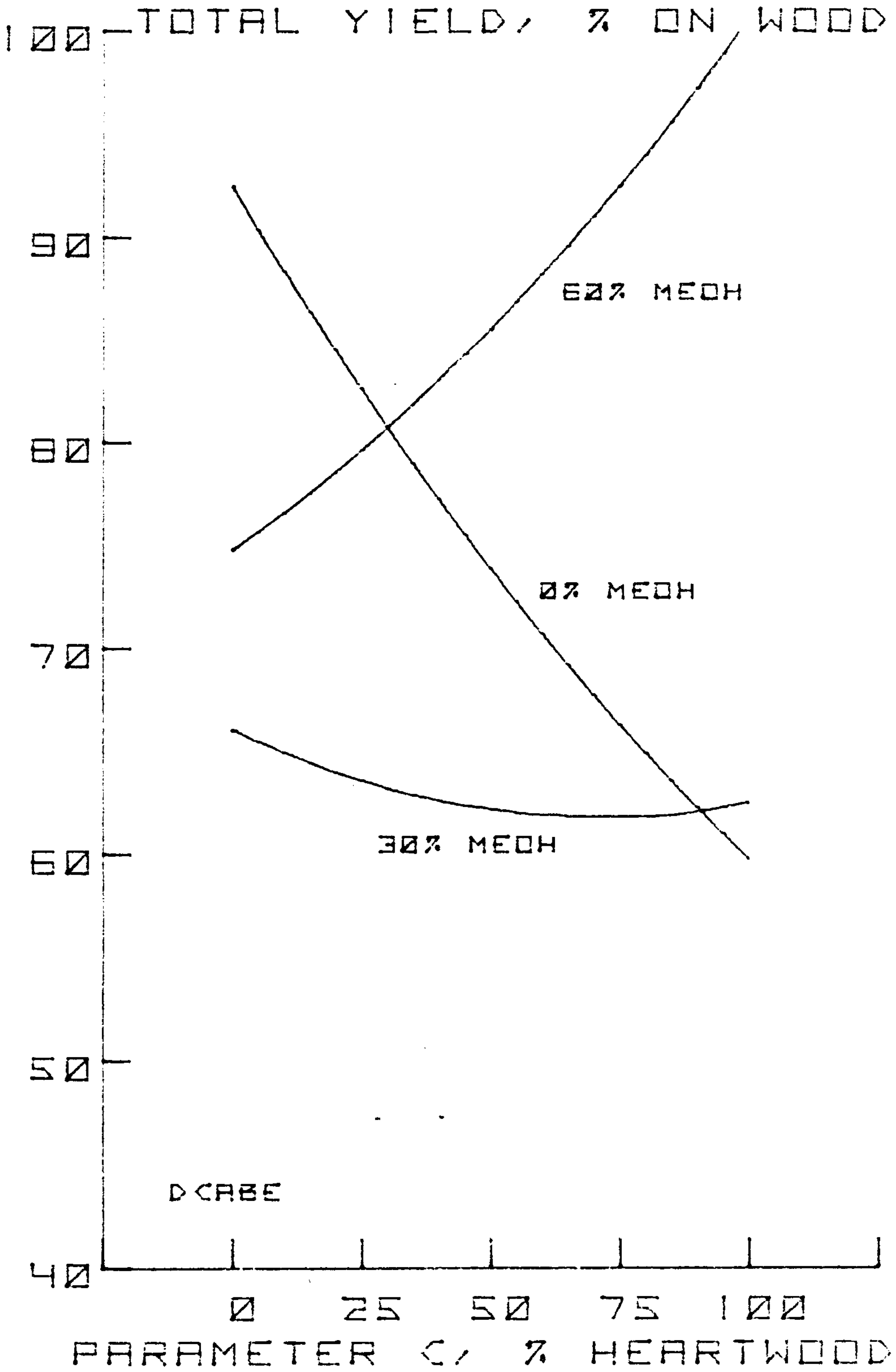


FIGURE 10 : Sulfite-Methanol pulp data illustrating kappa number vs. total yield with covariation of the % MeOH and the % Heartwood

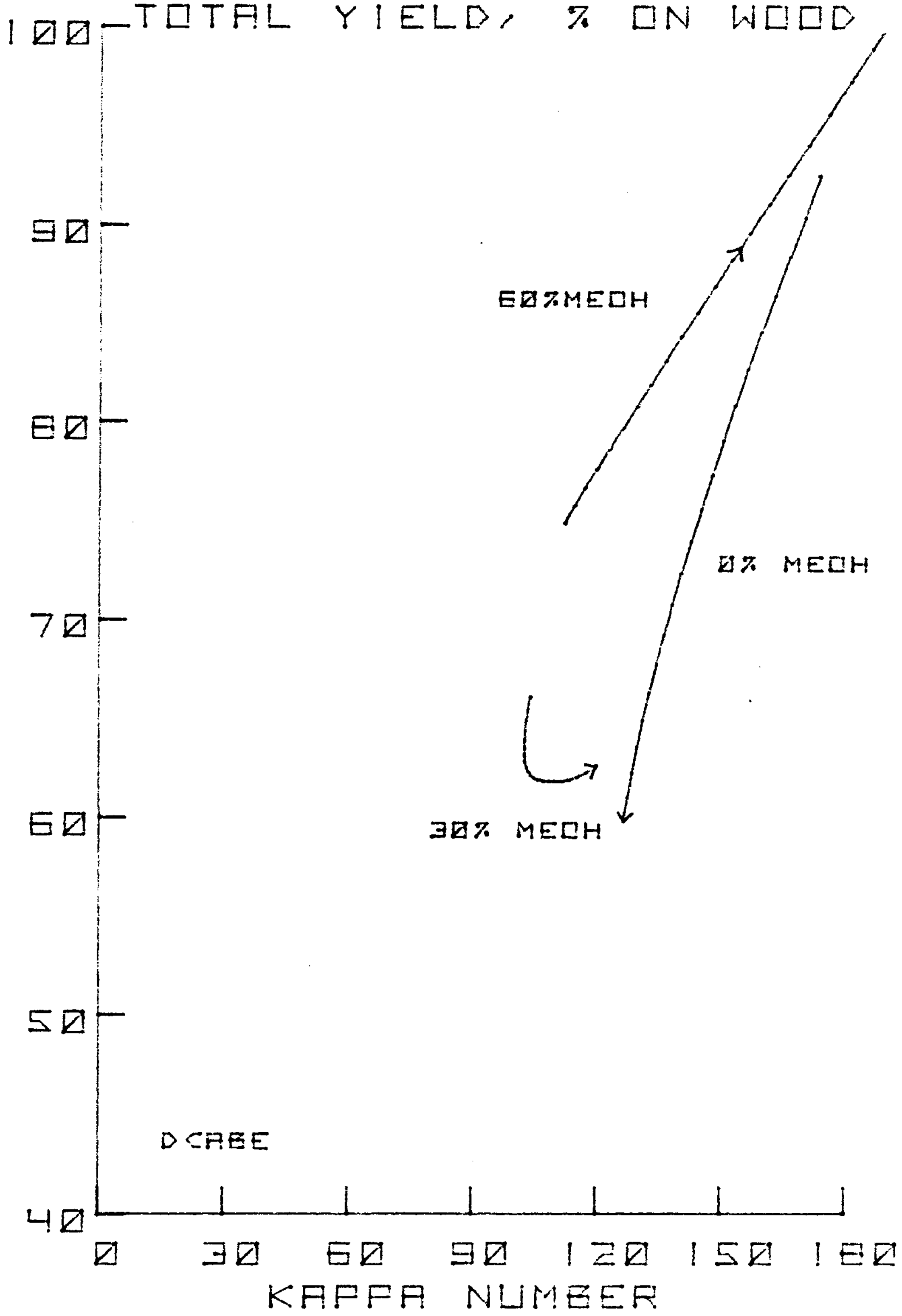


FIGURE 11 : Sulfite-Methanol pulp data illustrating Total yield vs. Deshive value with covariation of the % MeOH and the % Heartwood

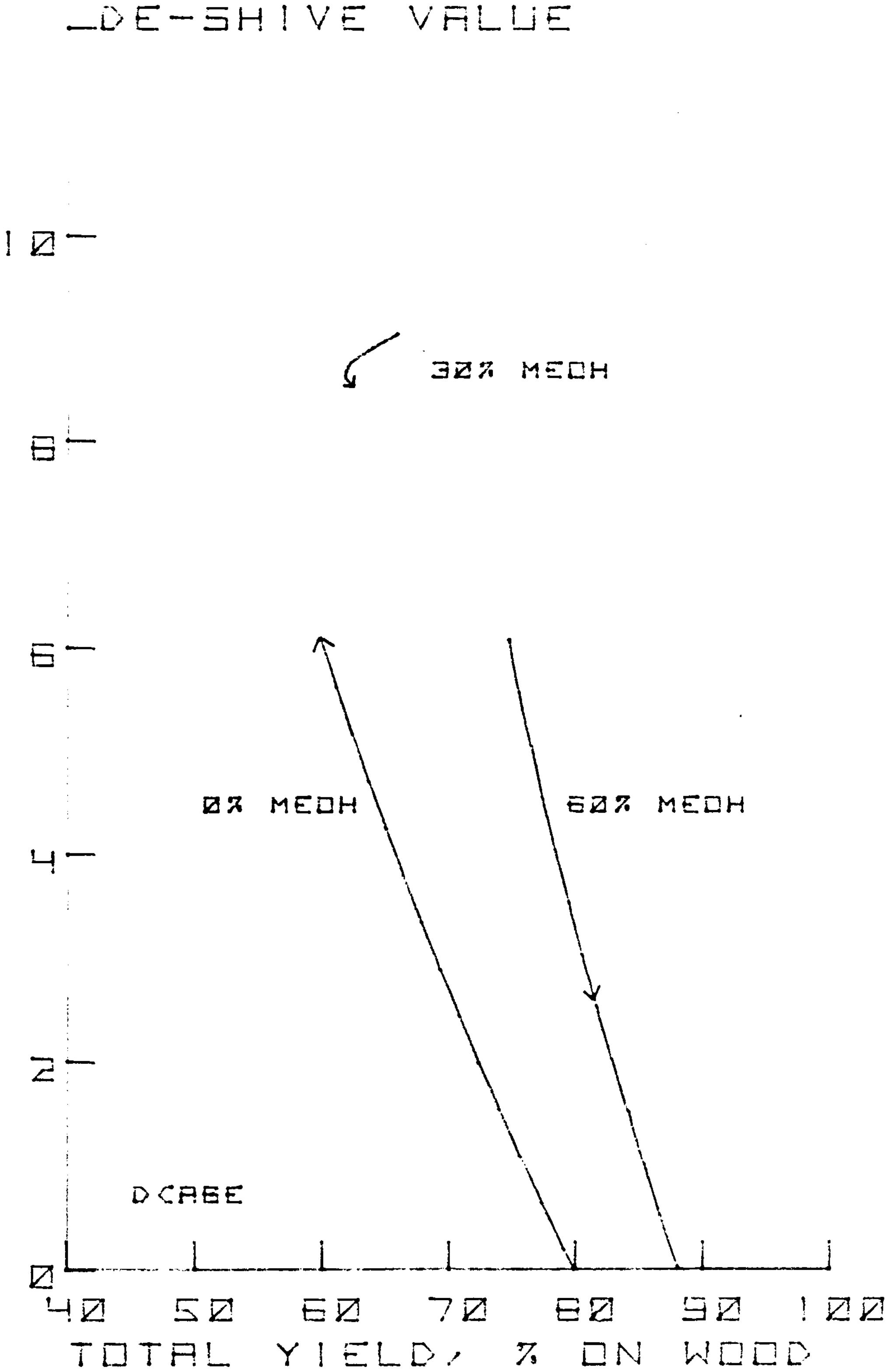


Table 7 shows the response of the three pulping systems to some of the variables chosen in the tube cooks. The table was made by going from levels 1 to 5 of the desired variable, keeping all the others constant at level 3.

As can be seen from Table 7, going from 100% sapwood to 100% heartwood causes a decrease in the soda-AQ kappa number of 13 points, a yield decrease of 2% and no change in the deshive value. It causes no change in the kraft-MeOH kappa, a decrease in yield of 3% and no change in the deshive value. In the sulfite-MeOH cooks increasing the percent heartwood caused a substantial increase in the kappa number, an increase in yield of 4%, and once again no change in the deshive value. These results show a minimal effect on the kappa number in the kraft-MeOH cooks when heartwood is added to the system. A moderate effect is shown in kappa number in the soda-AQ system and a very substantial effect is seen in the sulfite-MeOH system.

The reactions to the solvent ratio are very similar between the kraft-MeOH and sulfite-MeOH cooks. In each case a minimum in kappa number and yield with a maximum in deshive value is reached at level 3. This again shows that 30% solvent in the liquor at a 7:1 liquor to wood ratio pulps Douglas-fir the fastest in either a kraft or sulfite system modified with methanol.

In the soda-AQ case, varying the percent NaOH produces the expected results. When the percent NaOH is increased, the kappa and yield properties decrease while the deshive value increases, again indicating faster pulping with more NaOH in the system.

TABLE 7 : Pulping response of the process variables.

Process Variable	Cook Type	Level	Kappa Number	% Yield	Deshive Value
Percent Heartwood	Soda AQ	1	63	50	8
		3	63	50	9
		5	50	48	8
	Kraft MeOH	1	81	56	9
		3	81	55	9
		5	80	53	9
	Sulfite MeOH	1	82	60	9
		3	107	63	9
		5	127	64	9
Solvent Ratio	Kraft MeOH	1	136	70	1
		3	80	55	9
		5	96	56	8
	Sulfite MeOH	1	145	76	2
		3	107	62	9
		5	127	80	1
Percent NaOH	Soda AQ	1	100	58	2
		3	63	50	9
		5	30	45	9
Percent AQ	Soda AQ	1	88	52	8
		3	63	50	9
		5	45	48	10
	Kraft MeOH	1	100	57	9
		3	81	55	9
		5	74	54	9
Percent Free SO_2	Sulfite MeOH	1	140	80	3
		3	107	63	9
		5	52	51	8

The percent anthraquinone was varied in the soda-AQ and kraft-MeOH cooks. Table 7 shows that the addition of AQ indeed speeds up the pulping process because the kappa and yield values decrease as the percent AQ increases. The AQ makes no significant effect on the deshive values in these cooks.

Increasing the amount of free SO_2 in the sulfite-MeOH cooks gives a very substantial decrease in kappa number and yield while increasing the deshive value. This is not surprising since the lower the amount of free SO_2 in the cooking liquor, the slower the pulping rate.

Plotting deshive value vs. total yield showed some very interesting results which are listed below:

Cook Type	Yield at Deshive values ≥ 7
Soda-AQ	Up to 55% yield
Kraft-MeOH	Up to 60% yield
Sulfite-MeOH	Up to 65% yield

These results show that the sulfite-MeOH pulps deshive well up to 65% yield, the kraft-MeOH pulps deshive well up to 60% yield, and the soda-AQ pulps deshive well up to 55% yield. This indicates that the sulfite-MeOH pulps reach the fiber liberation point at a higher yield than the kraft-MeOH or soda-AQ pulps and so would not need as much refining as one of the alkaline pulps at a higher yield.

Figure 12 shows the kappa-yield regression curves for the soda-AQ, kraft-MeOH, and sulfite-MeOH cooks. The soda-AQ and kraft-MeOH curves have slopes that are very similar, with the kraft-MeOH curve showing close to a 2% higher yield than the soda-AQ cooks below a kappa number of 80. The sulfite-MeOH regression line has a very different slope than the other two. It shows a lower yield at a given kappa number than either the soda-AQ or the kraft-MeOH cooks below a kappa number of 60 but above that point the sulfite-MeOH curve shows a much better kappa-yield relationship. Each of the three cases shows a better kappa-yield relationship than industrial linerboard pulp which ranges from 52% to 57% yield and a kappa number of 90 to 120.

Figures 13 through 15 show the regression relations of Figure 12 but with 95% Working and Hotelling[24] confidence bounds on each regression line and showing the actual, measured points. Comparing Figures 13 and 14, the soda-AQ and kraft-MeOH regression lines, the confidence regions show a significant difference between the two lines below a kappa number of 100. Above that, there is no significant difference between the two lines. Also, in each of these two cases, the confidence regions of the lines are fairly narrow. This is not true of Figure 15, the confidence regions on the sulfite-MeOH regression line. In this case the 95% confidence region is much wider, especially at low kappa numbers where very few cooks were made. This indicates a much wider variation in the sulfite-MeOH cook results than for the soda-AQ or kraft-MeOH cook results.

FIGURE 12 : Kappa number vs. Total yield relationships for the three pulping systems

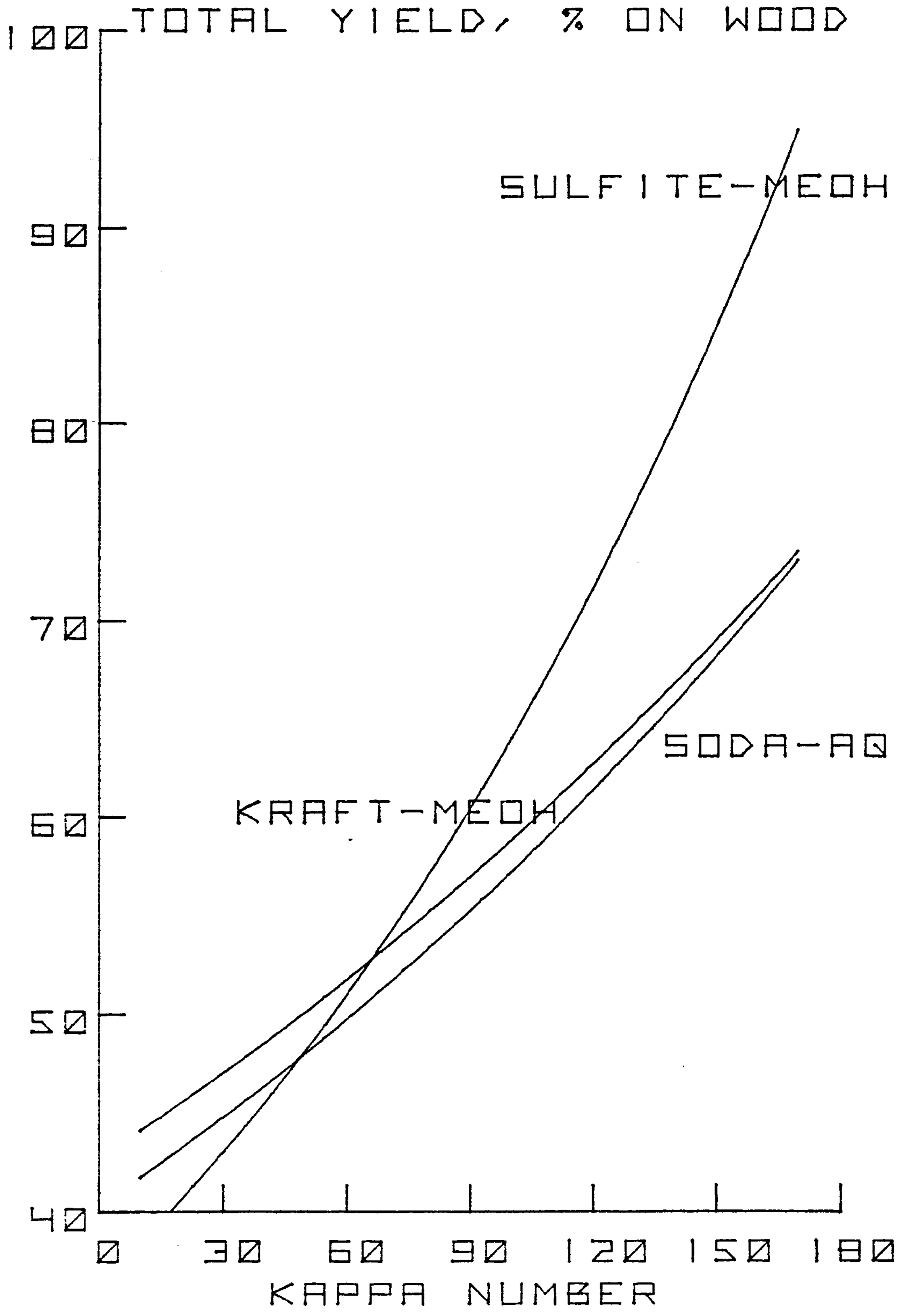


FIGURE 13 : Soda-Anthraquinone pulp data illustrating kappa number vs. Total yield with 95% confidence limits on the regression line

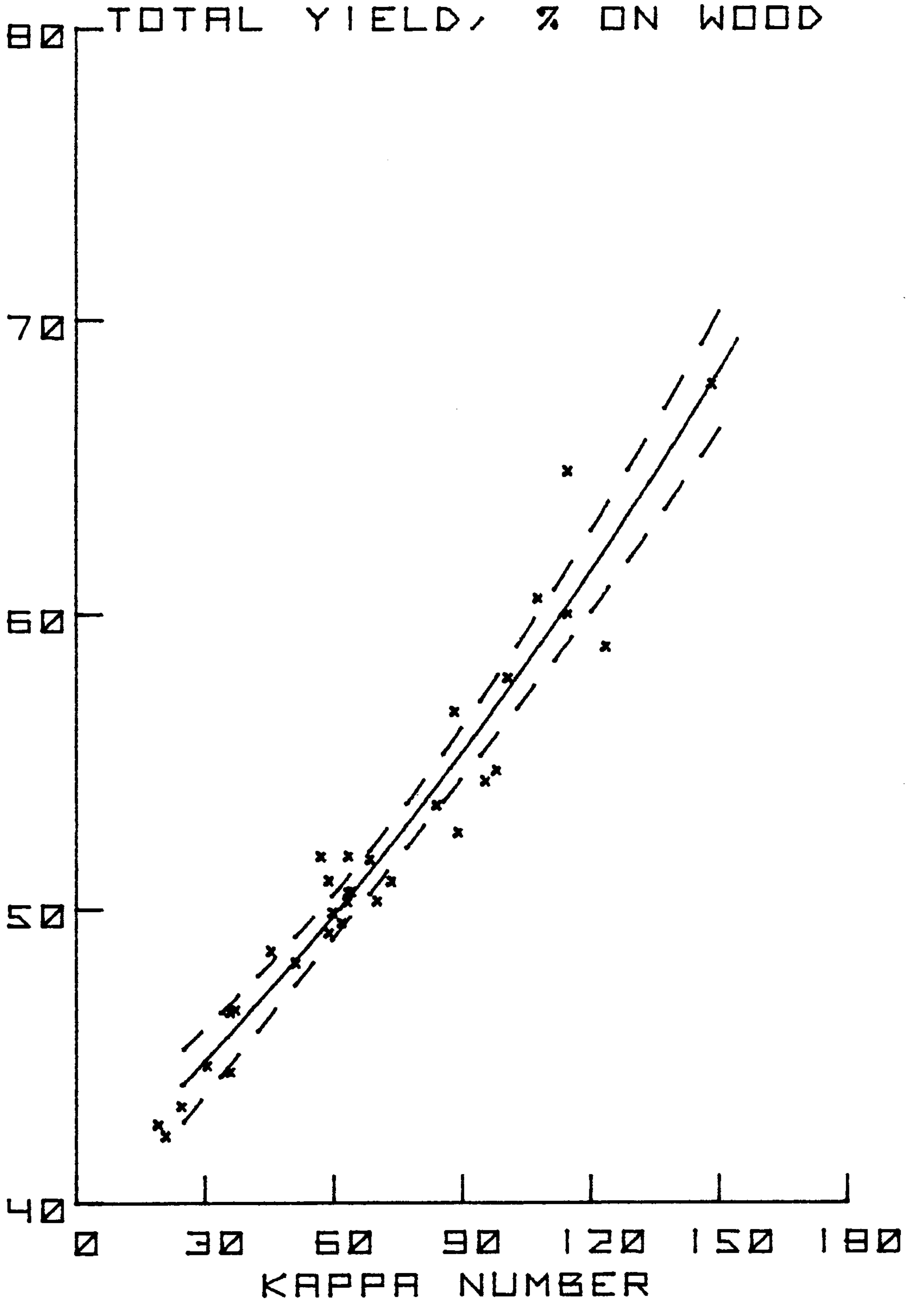


FIGURE 14 : Kraft-Methanol pulp data illustrating Kappa number vs. Total yield with 95% confidence limits on the regression line

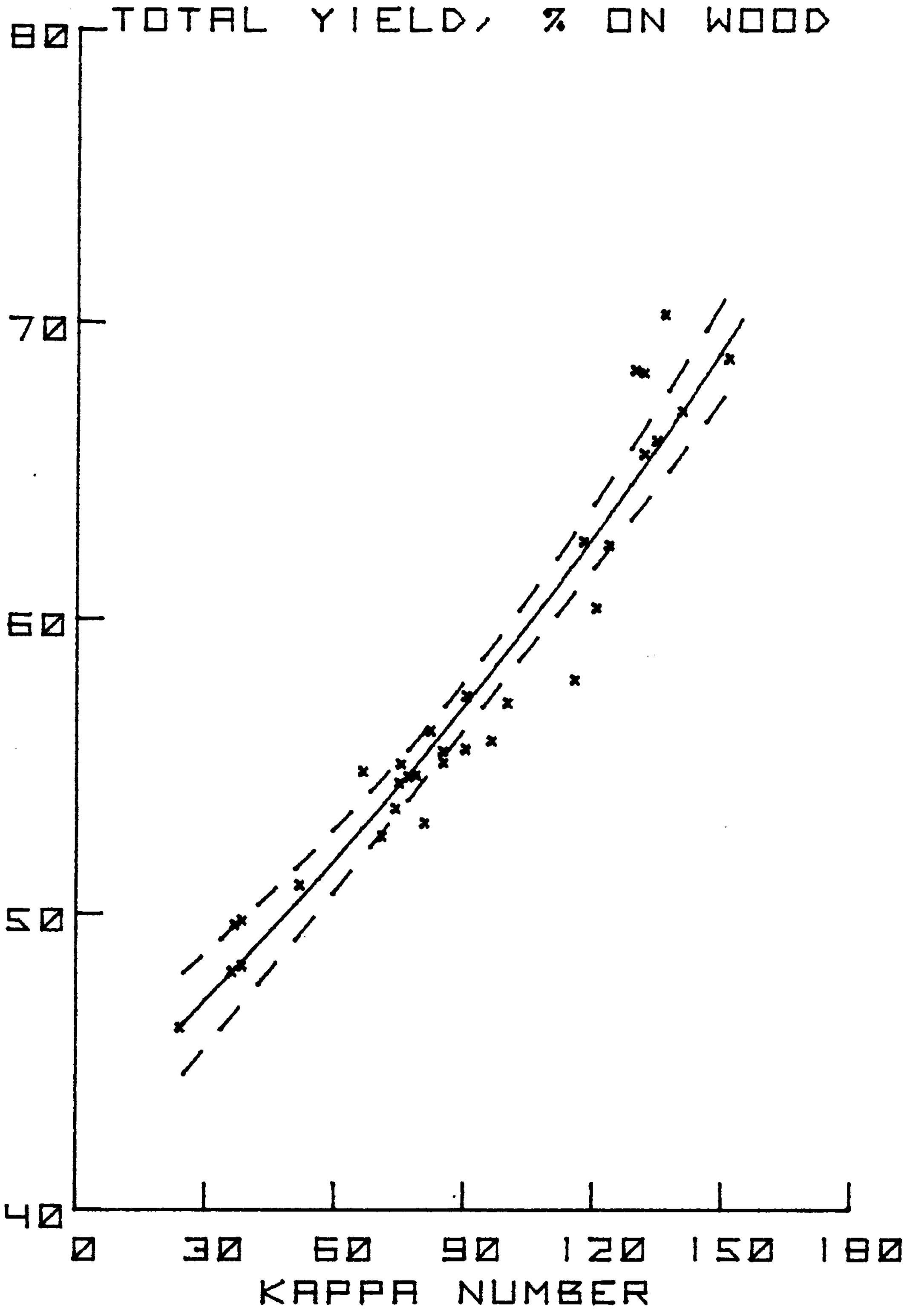
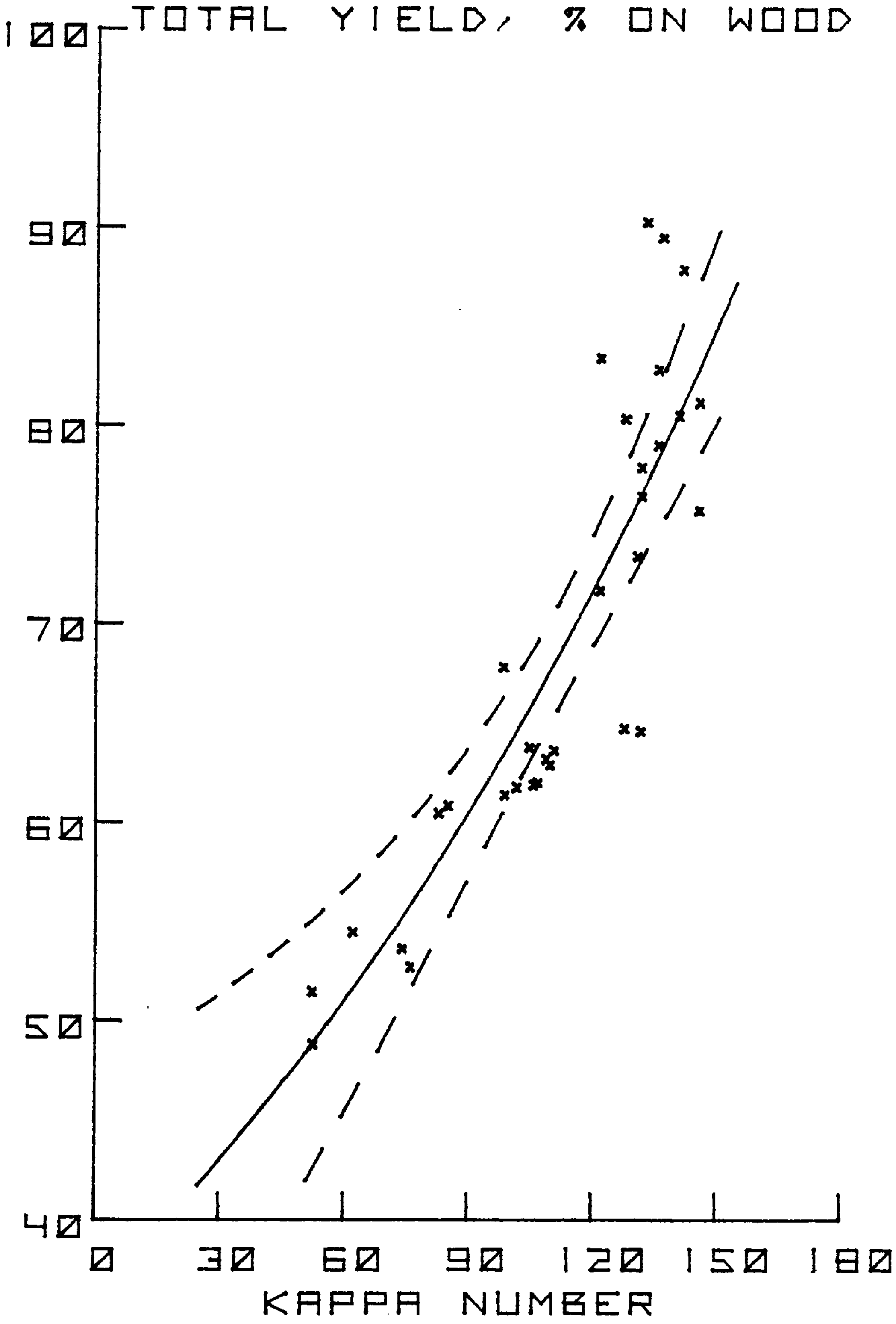


FIGURE 15 : Sulfite-Methanol pulp data illustrating Kappa number vs. Total yield with 95% confidence limits on the regression line



Strength Testing

For the purposes of strength testing, one traditional kraft cook was made along with three kraft-MeOH and three sulfite-MeOH cooks. No soda-AQ cooks were chosen due to low yields and poor sheet integrity. The conditions for the strength cooks were chosen from the tube cook series. The cooks were made in a one kilogram circulating liquor digester with a 7:1 liquor to wood ratio. The conditions are listed on Table 8 along with yield and kappa information. The kraft-MeOH cooks were made with no anthraquinone since it was determined by the tube cooks that it made very little difference on the outcome of the cooks. All the cooks listed on Table 8 were made with a 50-50 mixture of sapwood and heartwood, were cooked at 170^{o}C, and were brought up to temperature in 45 minutes. All but the Kraft-90, which was a traditional kraft cook, contained 30% methanol in the liquor.

Attempts were made to cook some chips by the sulfite-MeOH pulping system using 80% free SO_2 in the liquor. They pulped fine at 170^{o}C for up to 37.5 minutes at temperature, but when cooked for one hour the chips became burnt. This may be due to exhaustion of the bisulfite ion concentration.

Some interesting strength values were determined from the cooks listed in Table 8. The traditional kraft cook was used as the comparison for the other strength values to determine which would be usable for linerboard quality pulp. The strength values will be compared at handsheet bulk values of 1.6 and 1.8 cc/g which is right in the range of industrial linerboard. These strength values are listed on Tables 9 and 10.

The burst index for the kraft-MeOH cooks was very similar to that for the kraft cooks at a given bulk. The sulfite-MeOH cooks had burst indexes about 2/3 that of the kraft values. Because the burst index is the most important test for linerboard, the kraft-MeOH cooks look very promising for the high bursting strengths needed, but the sulfite-MeOH cooks look very poor. In the sulfite cooks, the burst index is the highest for the 40 minute cook while the burst indexes for the 60 and 80 minute cooks are almost identical.

The tear index for the 60 minute kraft-MeOH cook at a bulk of 1.8 cc/g is the same as for the water based kraft cook. The 15 minute kraft-MeOH tear index, though, is almost one-third lower. The tear strength of the sulfite-MeOH cooks at a bulk of 1.8 cc/g is just over half the value of the kraft cook. The tear index for the 15 minute kraft-MeOH cook at a bulk of 1.6 cc/g is the same as for the water based kraft cook. At a bulk of 1.8 cc/g, however, the kraft-MeOH tear index is lower. The sulfite-MeOH tear strengths are up to 80% of the kraft value. These results seem to indicate that the kraft-MeOH cooks are protecting the fibers, resulting in good bursting strength along with good tear strength.

The folding strength follows a similar pattern, with the kraft-MeOH strength very close to that of the kraft, but the sulfite-MeOH values are very much weaker, about one-third that of the water based kraft value.

TABLE 8 : Strength cook conditions and kappa-yield responses.

Cook Type	Time (min)	% Free SO_2	% Yield	Kappa Number
Kraft-water	90	NA	62	106
Kraft-MeOH	15	NA	52	60
Kraft-MeOH	37.5	NA	49	51
Kraft-MeOH	60	NA	50	52
Sulfite-MeOH	40	70	60	102
Sulfite-MeOH	60	70	54	65
Sulfite-MeOH	80	70	50	55

All cooks brought up to temperature in 45 minutes
cooked at 170°C
50-50 sapwood-heartwood

Kraft-water and Kraft-MeOH with 22.4% Active Alkali on o.d. wood
25% sulfidity

Sulfite-MeOH with 20% total SO_2 on o.d. wood

TABLE 9 : Strength results at 1.6 cc/g bulk

	1	2	3	4	5	6	7
Beating (#PFI rev./10)	904	2556	835	404	304	220	173
Canadian Std. Freeness (mls)	269	172	269	419	295	348	464
Brightness (%)	14.9	15.4	14.1	16.0	22.3	26.1	24.7
Burst Index (kPa·m^2/gram)	8.6	6.9	7.9	7.7	4.9	4.0	4.1
Tear Index (mN·m^2/gram)	10.5	10.4	11.9	14.0	7.7	8.5	8.7
Fold (# double folds)	1024	808	1006	1015	354	381	303
Breaking Length (meters)	11803	9257	10107	10642	8611	8040	7582
Stretch (%)	2.7	3.5	2.4	3.5	2.0	1.8	1.8
T.E.A. (joules/meter^2)	11.2	10.7	8.7	13.1	5.9	5.4	4.8

Column	Cook Type	Time	Kappa	% Yield
1	Kraft-water	90	51.6	50
2	Kraft-MeOH	15	106	62
3	Kraft-MeOH	37.5	60.3	52
4	Kraft-MeOH	60	45.7	49
5	Sulfite-MeOH	40	102	60
6	Sulfite-MeOH	60	65.4	54
7	Sulfite-MeOH	80	54.6	50

TABLE 10 : Strength results at 1.8 cc/g bulk

	1	2	3	4	5	6	7
Beating (#PFI rev./10)	140	1156	242	107	161	99	65
Canadian Std. Freeness (mls)	640	363	718	696	517	558	806
Brightness (%)	18.6	15.2	16.6	17.8	24.1	29.2	29.4
Burst Index (kPa·m^2/g)	5.6	6.0	6.1	5.6	4.1	3.3	3.2
Tear Index (mN·m^2/g	17.9	11.9	16.5	17.9	9.0	9.9	10.2
Fold (# double folds)	563	604	603	598	196	225	46
Breaking Length (meters)	8886	8713	9871	8531	7623	7022	6619
Stretch (%)	1.8	3.1	2.2	3.1	1.7	1.6	1.8
T.E.A. (joules/meter^2)	6.1	9.0	8.5	8.8	4.4	4.0	4.6

Column	Cook Type	Time	Kappa	%Yield
1	Kraft-water	90	51.6	50
2	Kraft-MeOH	15	106	62
3	Kraft-MeOH	37.5	60.3	52
4	Kraft-MeOH	60	45.7	49
5	Sulfite-MeOH	40	102	60
6	Sulfite-MeOH	60	65.4	54
7	Sulfite-MeOH	80	54.6	50

CONCLUSIONS

Listed below are the major conclusions found by this thesis.

1. Soda-Anthraquinone
    a. Pulped the slowest of the three systems.
    b. Deshive values ≥ 7 were obtained up to 55% yield.
    c. Addition of heartwood to the system lowered the kappa number 13 points.
    d. Increasing the amount of anthraquinone speeded the pulping process.

2. Kraft-Methanol
    a. Pulped the fastest of the three systems. The pulp was produced in less than half the time of a traditional kraft cook.
    b. Deshive values ≥ 7 were obtained at up to 60% yield.
    c. Addition of heartwood had no discernable effect on the kappa number.
    d. Increasing the amount of anthraquinone slightly increased the speed of pulping.
    e. The chips pulped the fastest at 30% (w/w) methanol in the liquor with a 7:1 liquor to wood ratio.
    f. Strength tests show methanol modified kraft pulp to be equivalent in strength to traditional kraft pulp.

3. Sulfite-Methanol
    a. Was the middle of the three systems in pulping speed.
    b. Deshive values ≥ 7 were obtained up to 65% yield.
    c. Addition of heartwood caused a 45 point increase in kappa number and a 4% increase in yield.
    d. Increasing the amount of free SO_2 in the liquor caused faster pulping but also caused the pulp to burn more easily.

e. The chips pulped the fastest with 30% (w/w) methanol in the liquor at a 7:1 liquor to wood ratio and the yields were the most stable when the ratio of sapwood to heartwood was varied.

f. Strength tests show the pulp is much weaker than a traditional kraft pulp.

g. The pulp came out of the digester a bright yellow which darkened on exposure to ultraviolet light.

The focus of this thesis was to determine alternative methods for the production of Douglas-fir linerboard quality pulp. High yields as well as strength properties were being sought. All three of these systems have points in their favor and points against them.

	+	-
Soda-AQ	No sulfur used	Low yields
	Can use present mills	Poor sheet quality
Kraft-MeOH	Strength equivalent to traditional kraft	Sulfur present
	Yield slightly higher than traditional kraft	New, fully enclosed mill would have to be built
	Very fast pulping	Higher digester pressure
Sulfite-MeOH	High yields	Sulfur present
	Good deshive value at the high yields	Yellow color
	Fast pulping	Low strengths
		New, fully enclosed mill would have to be built
		Higher digester pressure

From this work, a methanol modified kraft system looks the most promising as an alternative to traditional kraft pulp for linerboard. The pulp produced is very strong and the pulping is very fast.

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27. TAPPI Standard T236 m-60 : Kappa Number of Pulp.

28. TAPPI Standard T248 pm-74: Laboratory Beating of Pulp. (PFI Mill Method)

29. TAPPI Standard T277 m-58 : Freeness of Pulp.

30. TAPPI Standard T205 os-71: Forming Handsheets for Physical Tests of Pulp.

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APPENDICES

APPENDIX 1 : Definitions

BRIGHTNESS : Measures the "whiteness" of the paper. It is technically the percent reflectance of a thick pad of paper to an MgO standard at a wavelength of 457 nm under the conditions specified in TAPPI Standard T217 m-48.

BULK : The bulk is calculated as cubic centimeters per gram. It is the single sheet thickness in thousandths of a millimeter divided by the weight per unit area in grams per square meter (moisture free basis). The micrometer readings are taken according to TAPPI Standard T411 os-68 and the weight per unit area is calculated according to TAPPI Standard T220 os-71.

BURST : The bursting strength is the hydrostatic pressure in pascals, or kilonewtons per square meter required to produce rupture of the material when pressure is increased at a controlled constant rate through a rubber diaphram to a circular area, 30.5 mm in diameter. The area of the material under test is initially flat and held rigidly at the circumference but free to bulge during the test. The test is applied under the conditions specified in TAPPI Standard T403 os-74.

DESHIVE : The deshive value is an empirical procedure in which pulp handsheets are assigned a value from zero to ten.
zero : 100% shives (bundles of wood)
ten : no shives, a fully defibered pulp.

FREENESS : Canadian Standard Freeness is an empirical procedure which gives an arbitrary measure of the rate at which a suspension of three grams of pulp in one liter of water may be drained. This test is applied under the conditions specified in TAPPI Standard T227 m-58.

KAPPA : The kappa number is the number of milliliters of tenth-normal potassium permanganate solution consumed per gram of moisture-free pulp under the conditions specified in TAPPI Standard T236 m-60.

KRAFT PULPING : Pulping by use of an aqueous solution of NaOH and Na_2S. Has a better kappa-yield relationship than soda pulping. Pulps any species.

FOLD : The MIT folding endurance is defined as the number of double folds occurring until breakage of the specimen, with the specimen under 1 kg tension in an MIT fold tester.

TAPPI : TAPPI is the acronym for the Technical Association of the Pulp and Paper Industry.

TEAR : For the tearing strength, one or more sheets are torn together through a fixed distance by means of a pendulum using an Elmendorf type of tester. The work done in tearing is measured by the loss in potential energy of the pendulum. The scale is calibrated to indicate the average force exerted (work done divided by the total distance torn). The test is applied under the conditions specified in TAPPI Standard T414 ts-65.

TENSILE : The tensile breaking strength is the limiting resistance of a test specimen to a breaking force applied to its ends under the conditions specified in TAPPI Standard T404 os-74.

SODA PULPING : Pulping by use of an aqueous solution of NaOH. It was the first alkaline pulping system devised and will pulp any species.

SULFITE PULPING : Pulping by use of an aqueous solution of SO_2 in combination with a base, either Ca^{++}, Mg^{++}, NH_4^+, or Na^+. Easily pulps only wood free of phenolic extractives.

% YIELD : $$\frac{\text{Dry weight of pulp out of the digester}}{\text{Dry weight of wood into the digester}} \times 100$$

APPENDIX 2 : "Best" fit Regression Equations and Coefficients of Multiple Determination.

Soda-Anthraquinone Cooks

$$E\ (\text{Kappa}) = 235.97 - 50.16(X_1) - 6.30(X_5) + 5.69(X_6) - 4.40(X_9) - 3.32(X_{13}) + 1.67(X_{18})$$

$$R^2 = .93$$

$$E\ (\text{Yield}) = 108.03 - 16.74(X_1) - 3.30(X_2) + 1.65(X_3) - 4.37(X_4) - 3.98(X_5) + 1.32(X_6) + .50(X_7) + .61(X_{10}) - .73(X_{16}) + .32(X_{18}) + .48(X_{19})$$

$$R^2 = .98$$

$$E\ (\text{Deshive}) = -29.60 + 11.75(X_1) + 5.34(X_2) + 4.34(X_4) - .74(X_6) - .50(X_7) - .47(X_8) - .50(X_9) - .45(X_{10}) - .20(X_{15}) + .78(X_{16}) - .86(X_{18}) + .55(X_{19})$$

$$R^2 = .96$$

Kraft-Methanol Cooks

$$E\ (\text{Kappa}) = 268.74 - 18.98(X_1) - 50.05(X_4) - 5.10(X_7) + 7.57(X_{18})$$

$$R^2 = .96$$

$$E\ (\text{Yield}) = 110.92 - 5.99(X_1) - 8.34(X_2) - 11.25(X_4) + .84(X_{11}) - .17(X_{15}) + 1.70(X_{18})$$

$$R^2 = .92$$

$$E\ (\text{Deshive}) = -9.92 + 4.21(X_1) + 7.15(X_2) - 2.95(X_5) - .87(X_7) - .57(X_{11}) + .08(X_{15}) - .44(X_{18}) + 1.01(X_{19})$$

$$R^2 = .71$$

Sulfite-Methanol Cooks

$$E\ (\text{Kappa}) = 257.44 - 72.54(X_4) - 3.00(X_6) - 5.97(X_{12}) + 4.17(X_{14}) + 9.75(X_{16}) - 2.58(X_{17}) + 9.62(X_{18}) - 4.66(X_{19})$$

$$R^2 = .74$$

$$E\ (\text{Yield}) = 153.35 - 8.65(X_1) - 31.48(X_4) - 5.12(X_5) + 1.31(X_{11}) - 3.34(X_{12}) + 3.09(X_{16}) + 4.18(X_{18})$$

$$R^2 = .85$$

$$E\ (\text{Deshive}) = -36.68 + 11.00(X_1) + 10.79(X_4) + 4.26(X_5) - 1.10(X_6) - .56(X_{10}) - .68(X_{11}) + .94(X_{12}) + .73(X_{13}) - 1.36(X_{16}) + .39(X_{17}) - 1.85(X_{18})$$

The E () stands for the expected value of the property in the brackets. The X values are described on Table 5.

APPENDIX 3

TABLE 11 : Soda-Anthraquinone 32 cook series pulping response.

Cook	Parameters					Kappa	%	Bright-	Deshive
No.	A	B	C	D	E	Number	Yield	ness	Value
1	3	3	3	3	3	58.1	50.8	25.8	9
2	3	3	3	3	3	62.4	50.1	27.2	8
3	3	3	3	3	3	69.4	50.1	26.4	9
4	3	3	3	3	3	62.7	51.6	26.4	8
5	3	3	3	3	3	63.4	50.5	26.3	10
6	3	3	3	3	3	61.1	49.4	26.4	9
7	1	3	3	3	3	148	67.7	18.7	3
8	5	3	3	3	3	18.3	42.6	35.8	9
9	3	1	3	3	3	94.7	54.2	21.2	6
10	3	5	3	3	3	35.1	46.4	30.0	8
11	3	3	1	3	3	62.6	50.4	24.7	8
12	3	3	5	3	3	50.4	48.0	27.0	8
13	3	3	3	1	3	100	57.7	18.9	2
14	3	3	3	5	3	29.8	44.6	35.5	9
15	3	3	3	3	1	88.4	52.5	24.3	8
16	3	3	3	3	5	44.6	48.4	29.7	10
17	2	2	2	2	4	107	60.4	20.3	2
18	2	2	2	4	2	123	58.7	21.0	3
19	2	2	4	2	2	114	64.7	16.2	0
20	2	2	4	4	4	97.4	54.6	22.3	8
21	2	4	2	2	2	114	59.9	20.1	5
22	2	4	2	4	4	83.3	53.4	26.0	9
23	2	4	4	2	4	87.5	56.6	21.2	4
24	2	4	4	4	2	72.7	50.8	26.5	8
25	4	2	2	2	2	67.7	51.6	25.6	8
26	4	2	2	4	4	36.3	46.4	33.9	9
27	4	2	4	2	4	56.2	51.7	24.8	4
28	4	2	4	4	2	35.2	44.3	32.0	9
29	4	4	2	2	4	58.0	49.1	27.2	9
30	4	4	2	4	2	23.8	43.2	36.5	10
31	4	4	4	2	2	58.9	49.7	25.4	7
32	4	4	4	4	4	20.1	42.2	35.5	9

TABLE 12 : Kraft-methanol 32 cook series pulping response.

Cook No.	Parameters A B C D E	Kappa Number	% Yield	Bright-ness	Deshive Value
1	3 3 3 3 3	89.6	55.4	22.4	8
2	3 3 3 3 3	78.1	54.6	24.6	9
3	3 3 3 3 3	84.4	55.4	24.0	8
4	3 3 3 3 3	74.6	54.9	24.6	8
5	3 3 3 3 3	76.3	54.5	24.0	9
6	3 3 3 3 3	89.8	57.2	23.5	9
7	1 3 3 3 3	151	68.7	18.9	3
8	5 3 3 3 3	23.5	46.0	33.6	10
9	3 1 3 3 3	131	68.2	17.2	2
10	3 5 3 3 3	51.1	50.9	26.6	9
11	3 3 1 3 3	81.5	56.1	25.2	9
12	3 3 5 3 3	80.2	52.9	22.6	9
13	3 3 3 1 3	136	70.1	17.9	1
14	3 3 3 5 3	95.8	55.7	18.2	8
15	3 3 3 3 1	99.5	57.0	22.0	9
16	3 3 3 3 5	74.3	54.3	23.4	9
17	2 2 2 2 4	140	66.9	17.8	3
18	2 2 2 4 2	129	68.3	15.1	1
19	2 2 4 2 2	131	65.4	18.9	7
20	2 2 4 4 4	134	65.9	16.7	6
21	2 4 2 2 2	123	62.3	20.2	7
22	2 4 2 4 4	117	62.5	19.4	8
23	2 4 4 2 4	115	57.8	20.7	8
24	2 4 4 4 2	120	60.2	18.1	7
25	4 2 2 2 2	84.5	55.0	25.9	9
26	4 2 2 4 4	65.8	54.7	22.9	9
27	4 2 4 2 4	73.3	53.4	25.0	9
28	4 2 4 4 2	70.2	52.5	22.5	9
29	4 4 2 2 4	37.8	49.6	31.7	8
30	4 4 2 4 2	36.2	49.5	27.8	9
31	4 4 4 2 2	35.5	47.9	31.5	9
32	4 4 4 4 4	37.8	48.1	25.6	9

TABLE 13 : Sulfite-methanol 32 cook series pulping response.

Cook No.	Parameters A B C D E	Kappa Number	% Yield	Brightness	Deshive Value
1	3 3 3 3 3	110	63.5	41.6	9
2	3 3 3 3 3	105	61.7	43.9	9
3	3 3 3 3 3	108	63.0	43.7	8
4	3 3 3 3 3	109	62.7	45.7	9
5	3 3 3 3 3	104	63.6	39.4	9
6	3 3 3 3 3	106	61.8	43.3	8
7	1 3 3 3 3	121	83.2	36.0	0
8	5 3 3 3 3	51.8	48.6	25.9	9
9	3 1 3 3 3	131	76.2	38.6	2
10	3 5 3 3 3	61.4	54.3	46.3	9
11	3 3 1 3 3	82.1	60.3	50.7	9
12	3 3 5 3 3	127	64.5	36.6	9
13	3 3 3 1 3	145	75.5	33.4	2
14	3 3 3 5 3	127	80.2	38.7	1
15	3 3 3 3 1	140	80.3	33.9	3
16	3 3 3 3 5	51.7	51.3	48.5	8
17	2 2 2 2 4	130	73.2	41.0	1
18	2 2 2 4 2	132	90.1	39.6	0
19	2 2 4 2 2	145	81.0	32.6	0
20	2 2 4 4 4	135	82.6	33.7	0
21	2 4 2 2 2	136	89.3	38.0	0
22	2 4 2 4 4	131	77.7	46.6	3
23	2 4 4 2 4	131	64.4	38.2	4
24	2 4 4 4 2	141	87.7	33.1	0
25	4 2 2 2 2	98.1	61.2	35.8	8
26	4 2 2 4 4	84.4	60.7	47.0	9
27	4 2 4 2 4	75.4	52.6	42.4	7
28	4 2 4 4 2	135	78.8	30.9	2
29	4 4 2 2 4	121	71.5	36.5	3
30	4 4 2 4 2	97.7	67.6	40.7	9
31	4 4 4 2 2	73.4	53.5	37.0	9
32	4 4 4 4 4	101	61.6	40.7	8

APPENDIX 4

TABLE 14 : Kraft-water 90 minute strength data.

Original Data

Yield: 50.5% Kappa: 51.6

Interval	1	2	3	4
Basis Weight (g/m^2)	61.4	53.6	56.9	56.9
CSF (mls)	696	572	394	240
Beating ($\frac{\#\text{PFI rev.}}{10}$)	100	300	500	700
Brightness (%)	19.4	16.8	15.7	16.1
Bulk (cc/g)	1.84	1.67	1.69	1.65
Density (g/cc)	0.54	0.60	0.59	0.61
Burst Index ($kPa \cdot m^2/g$)	5.1	7.4	7.2	8.0
Tear Index ($mN \cdot m^2/g$)	19.3	13.4	13.4	12.5
Fold (# dbl. folds)	496	719	820	1035
Breaking Length (meters)	8310	10515	10905	10997
Stretch (%)	1.7	2.4	2.4	2.3
T.E.A. ($joules/m^2$)	5.1	9.2	9.6	9.6

TABLE 15 : Kraft-methanol 15 minute strength data.

Original Data

Yield: 61.8% Kappa: 106

Interval	1	2	3	4
Basis Weight (g/m^2)	51.7	55.2	56.5	55.3
CSF (mls)	690	613	522	336
Beating ($\frac{\#\text{PFI rev.}}{10}$)	250	500	750	1000
Brightness (%)	14.8	15.0	14.8	15.3
Bulk (cc/g)	2.18	1.97	1.96	1.82
Density (g/cc)	0.46	0.51	0.51	0.55
Burst Index ($kPa \cdot m^2/g$)	4.4	4.9	5.4	6.0
Tear Index ($mN \cdot m^2/g$)	14.2	14.0	13.0	11.5
Fold (# dbl. folds)	253	377	391	635
Breaking Length (meters)	7658	8059	8508	8602
Stretch (%)	2.4	2.6	2.9	3.1
T.E.A. ($joules/m^2$)	5.8	7.0	8.3	8.8

TABLE 16: Kraft-methanol 37.5 minute strength data.

Original Data

Yield: 51.8%   Kappa: 60.3

Interval	1	2	3	4
Basis Weight (g/m^2)	64.6	61.8	58.4	55.6
CSF (mls)	647	542	313	170
Beating ($\frac{\#\text{PFI rev.}}{10}$)	250	500	750	1000
Brightness (%)	17.2	14.3	14.3	14.1
Bulk (cc/g)	1.78	1.71	1.62	1.56
Density (g/cc)	0.56	0.59	0.62	0.64
Burst Index ($kPa \cdot m^2/g$)	6.2	7.0	8.0	8.0
Tear Index ($mN \cdot m^2/g$)	15.7	14.8	12.3	10.8
Fold (# dbl. folds)	578	869	1038	1005
Breaking Length (meters)	9991	10052	9508	10563
Stretch (%)	2.1	2.5	2.3	2.4
T.E.A. ($joules/m^2$)	7.6	10.3	7.6	9.0

TABLE 17: Kraft-methanol 60 minute strength data.

Original Data

Yield: 48.9% Kappa: 45.7

Interval	1	2	3	4
Basis Weight (g/m^2)	60.8	61.2	58.1	60.3
CSF (mls)	686	524	440	220
Beating ($\frac{\#\text{PFI rev.}}{10}$)	100	300	500	700
Brightness (%)	18.0	16.2	15.7	15.5
Bulk (cc/g)	1.80	1.66	1.54	1.53
Density (g/cc)	0.55	0.60	0.65	0.65
Burst Index ($kPa \cdot m^2/g$)	5.4	7.4	8.2	8.4
Tear Index ($mN \cdot m^2/g$)	18.2	14.8	12.7	13.1
Fold (# dbl. folds)	582	901	1186	1101
Breaking Length (meters)	8337	10300	11359	11095
Stretch (%)	3.0	3.5	3.6	3.8
T.E.A. ($joules/m^2$)	9.2	10.8	14.2	15.1

TABLE 18 : Sulfite-methanol 40 minute strength data.

Original Data

Yield: 59.8% Kappa: 102

Interval	1	2	3	4
Basis Weight (g/m^2)	51.6	54.6	50.2	53.2
CSF (mls)	666	472	329	157
Beating ($\frac{\#\text{PFI rev.}}{10}$)	100	200	300	400
Brightness (%)	24.8	25.0	22.8	20.3
Bulk (cc/g)	1.96	1.70	1.62	1.52
Density (g/cc)	0.51	0.59	0.62	0.66
Burst Index ($kPa \cdot m^2/g$)	3.4	4.7	4.9	5.0
Tear Index ($mN \cdot m^2/g$)	10.0	8.7	7.6	7.3
Fold (# dbl. folds)	90	266	260	485
Breaking Length (meters)	6762	8020	8990	8695
Stretch (%)	1.4	1.9	2.0	2.0
T.E.A. ($joules/m^2$)	3.2	5.3	6.0	6.1

TABLE 19: Sulfite-methanol 60 minute strength data.

Original Data

Yield: 54.1% Kappa: 65.4

Interval	1	2	3	4
Basis Weight (g/m^2)	54.7	59.0	54.6	55.2
CSF (mls)	722	424	215	110
Beating ($\frac{\#\text{PFI rev.}}{10}$)	50	200	350	500
Brightness (%)	31.5	26.4	26.4	21.2
Bulk (cc/g)	1.98	1.61	1.49	1.40
Density (g/cc)	0.51	0.62	0.67	0.71
Burst Index ($kPa \cdot m^2/g$)	2.6	4.2	4.4	4.7
Tear Index ($mN \cdot m^2/g$)	11.1	8.5	8.0	7.0
Fold (# dbl. folds)	108	303	498	557
Breaking Length (meters)	6048	8314	8345	9071
Stretch (%)	1.3	2.0	1.9	2.0
T.E.A. ($joules/m^2$)	2.5	6.2	5.6	6.8

TABLE 20 : Sulfite-methanol 80 minute strength data.

Original Data

Yield: 49.6% Kappa: 54.6

Interval	1	2	3	4
Basis Weight (g/m^2)	642	442	272	157
Beating ($\frac{\#\text{PFI rev.}}{10}$)	100	200	300	400
Brightness (%)	28.0	22.4	23.1	20.5
Bulk (cc/g)	1.71	1.58	1.47	1.44
Density (g/cc)	0.58	0.63	0.68	0.70
Burst Index ($kPa\cdot m^2/g$)	3.6	4.3	4.6	4.8
Tear Index ($mN\cdot m^2/g$)	9.7	8.3	7.8	7.6
Fold (# dbl. folds)	169	310	486	508
Breaking Length (meters)	6893	8088	7831	8484
Stretch (%)	1.8	1.8	1.8	1.7
T.E.A. ($joules/m^2$)	4.6	5.1	5.0	5.0