

Hemicellulose retention during kraft pulping

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ABSTRACT *Kraft pulping experiments were conducted for red spruce in a well-controlled laboratory digester. These experiments were performed as a central composite, statistically designed set. Wood and pulp samples were analyzed for extractives, soluble and insoluble lignin, component sugars, uronic acids, and acetyl groups. These data were used to estimate the polymeric composition of the wood and pulp. Composition data were fit to multiple regression equations.*

Conditions that favor retention of hemicellulose polymers are low temperature, low effective alkali charge, and low chip thickness. The analytical equations show that there are optimum cooking conditions that maximize hemicellulose retention when pulping to a target kappa number.

KEYWORDS

Fibers
Hemicellulose
Kraft pulping
Pulping
Retention

The retention of the hemicellulose polymers galactoglucomannan and arabinoglucuronoxylan during alkaline pulping is important. Hemicellulose retention increases pulp yield, improves pulp strength, makes an impact on water affinity, and affects fiber quality.

The quality of the fibers and their use in papermaking can be approached from several different perspectives. One approach may be dominated by fiber morphology, another by paper physics, and a third by pure chemistry. Therefore, a thorough understanding of the boundaries of a variety of approaches may offer the best opportunity to optimize the use of various fiber supplies.

The pure chemical approach offers a way for us to conceptualize the impact on pulp quality of various raw materials and digester time and

temperature control. With this premise, it is possible to focus on the chemical composition of fibers as an avenue to optimize the pulping process.

On one extreme, there is a growing body of evidence that points to the importance of the molecular weight of various cellulose and hemicellulose biopolymers. A somewhat less detailed and more easily conceptualized approach is the study of the absolute concentrations of cellulose and various hemicelluloses as a percentage of wood, pulp, or residual pulping liquor. This approach has been used successfully by a number of researchers to describe the relationship of chemical composition of pulps to ease of refining, sorption of water by the fiber, and the development of strength properties.

Early researchers (1, 2) realized

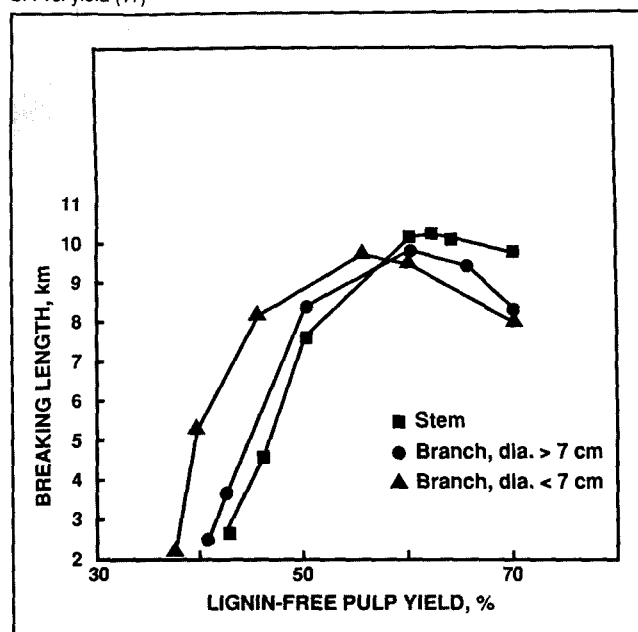
how important hemicellulose polymers are to pulp and paper properties. Although hemicelluloses are distributed throughout the fiber cell wall, they are concentrated on the outer surface of microfibrils (3, 4). Therefore, hemicelluloses are important in determining the chemical interaction between fibers, water, and a variety of chemicals used in the papermaking process. McIntosh (5) and Spiegelberg (6) studied the effect of hemicellulose on the tensile, bonding, and mechanical properties of southern pines. The removal of hemicellulose was shown to reduce breaking stress, the modulus of elasticity, yield point stress, and work to rupture. From the perspective of pulp processing, it is important to understand the pulping conditions that promote the retention of various hemicelluloses.

1. Chemical loss (% on wood) during kraft cooking, from Matthews (8)

	Lignin	Arabino- glucurono- xylan	Galacto- gluco- mannan	Cellu- lose
Low temp. loss ^a	4.3	0.0	9.1	3.5
High temp. loss ^b	19.1	2.3	2.2	0.4

^aFrom the beginning of the cook to 150°C, reached after 72 min.
^bFrom 150°C to 170°C in 18 min, plus 90 min at 170°C.

1. Breaking length of holocellulose pulps beaten to a freeness of 50° SR vs. yield (11)



Related literature

The principal softwood hemicelluloses include galactoglucomannan, arabinoglucuronoxylan, and even arabinogalactans in some special cases such as in larch. The selective dissolution of these hemicelluloses is demonstrated by the early work of Aurell and Hartler (7) and later by Matthews (8).

Aurell and Hartler conducted pulp- ing experiments on pine to a target kappa number by simultaneously increasing the effective alkali charge to the digester and by decreasing the time at maximum temperature (170°C). An increase in the charge of alkali in kraft pulping of pine resulted in a lower pulp yield at a given kappa number and shorter cooking time. The drop in the pulp yield was the result of a decrease in the yield of arabinoglucuronoxylan and galactoglucomannans in the pulp. Also, there was a change in the ratio of galactoglucomannan to arabinoglucuronoxylan as the effective alkali increased. Furthermore, as a result of the increase in the charge of the alkali, the pulp was more difficult to beat. Maximum breaking length and burst factor decreased, whereas the tear factor at a certain breaking length increased.

In a study involving slash pine, Matthews (8) demonstrated high losses of the galactoglucomannan

polymers at low temperatures and retention at high temperatures (Table I). The opposite behavior was observed for the arabinoglucuronoxylan polymer, with retention at low temperature but higher losses at high temperature. Similar results were observed for lignin (Table I). Matthews concluded that, as a percentage of the wood, a more significant portion of the total loss in hemicellulose occurs in the lower temperature regimes, or in the earlier stages of the cook.

This uneven loss was confirmed by Kondo and Sarkanen (9) who estimated that as much as 7% of the weight of wood in the form of hemicelluloses was directly dissolved during the initial stage of the pulping process. This compares favorably with the low temperature data of Matthews (8). Kondo and Sarkanen also suggested that once the initial dissolution of hemicelluloses has occurred, subsequent losses would occur via peeling reactions, as more hemicellulose becomes available to chemical attack.

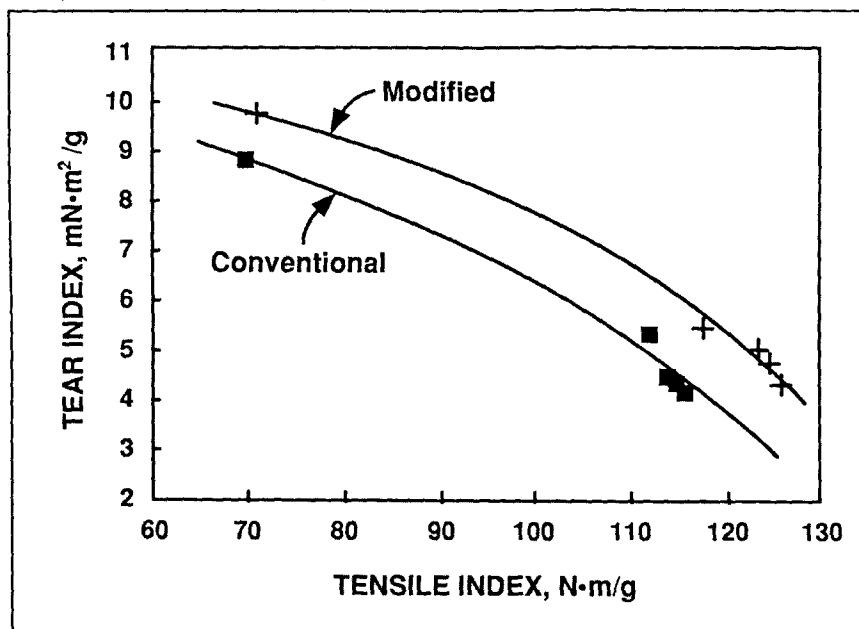
This hypothesis was reached indirectly in an earlier study by Dillen and Noreus (10). In their work on a series of short-duration cooks, these authors suggested that losses of hemicelluloses would be quite high in the earlier stages of the cooks. Presumably, this early loss involves those hemicelluloses that are directly dissolved. Dillen and Noreus also suggest that

the molecular weight of the components lost in the early stages would be high as well. Again, this would be consistent with direct dissolution as opposed to fragment losses from peeling reactions. Not only should the quantity of dissolved material diminish as the cook progresses, then, but the molecular weight of that material should diminish as well. This development was also observed by Dillen and Noreus.

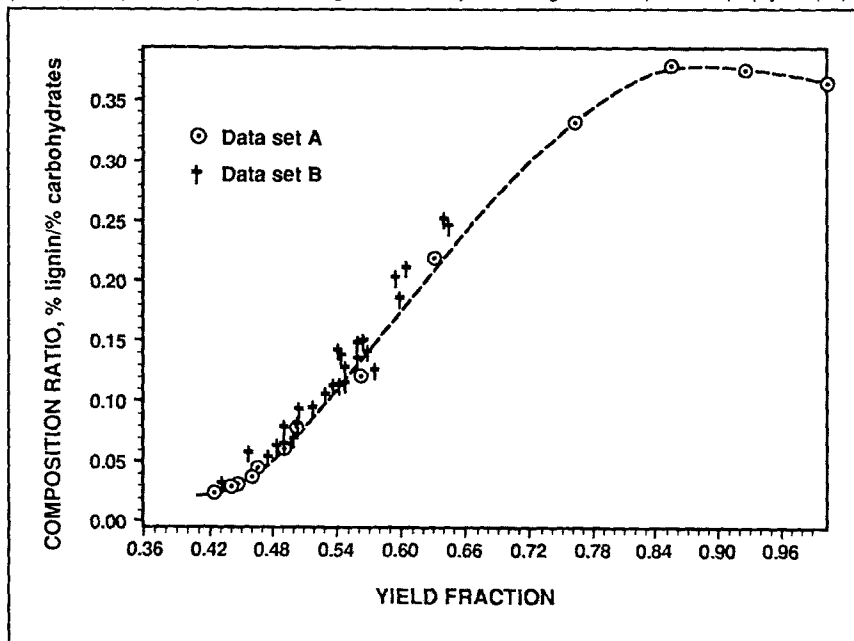
There are a number of ways in which the presence or absence of hemicelluloses can affect either the refinability of the pulp or the properties of the papers that are made with these pulps. One of the more desirable effects of increased hemicellulose retention is its positive impact on strength properties. Fiserova, Opale- na, and Farkas (11) prepared a number of holocellulose pulps at different yields with variations in the hemicellulose content. Pulps were prepared from the stem and branches of fast-growing poplar wood. Holocellulose pulps were first produced, and the pulps were then exposed to various amounts of sodium hydroxide at various concentrations.

In Fig. 1, breaking length vs. pulp yield is plotted for three brownstock pulps with varying hemicellulose content, based on the data of Fiserova *et al.* (11). One explanation of the results would suggest that breaking

2. Curves of tear strength vs. tensile for northern softwood pulped by the conventional kraft process and by modified continuous cooking (13)



3. Pulp composition (as the ratio of lignin to carbohydrate weight fraction) vs. total pulp yield (15)



length improved with an apparent increase in hemicellulose content. It is difficult with the data given to establish the mechanism of strength improvement. Was strength improved through improved specific bond strength, as a result of hemicellulose content on the surface of the microfibrils? Or did the strength improve because more water was associated with the fiber, which resulted in

improved swelling that subsequently improved the pliability of the fibers? Either mechanism could result in an improvement in the breaking length.

Sandstrom, Lindberg, and Teder (12) combine the concepts of pulping selectivity and strength as represented by pulp viscosity. They present a mathematical model for continuous digesters that describes different ways of delignifying pulps while

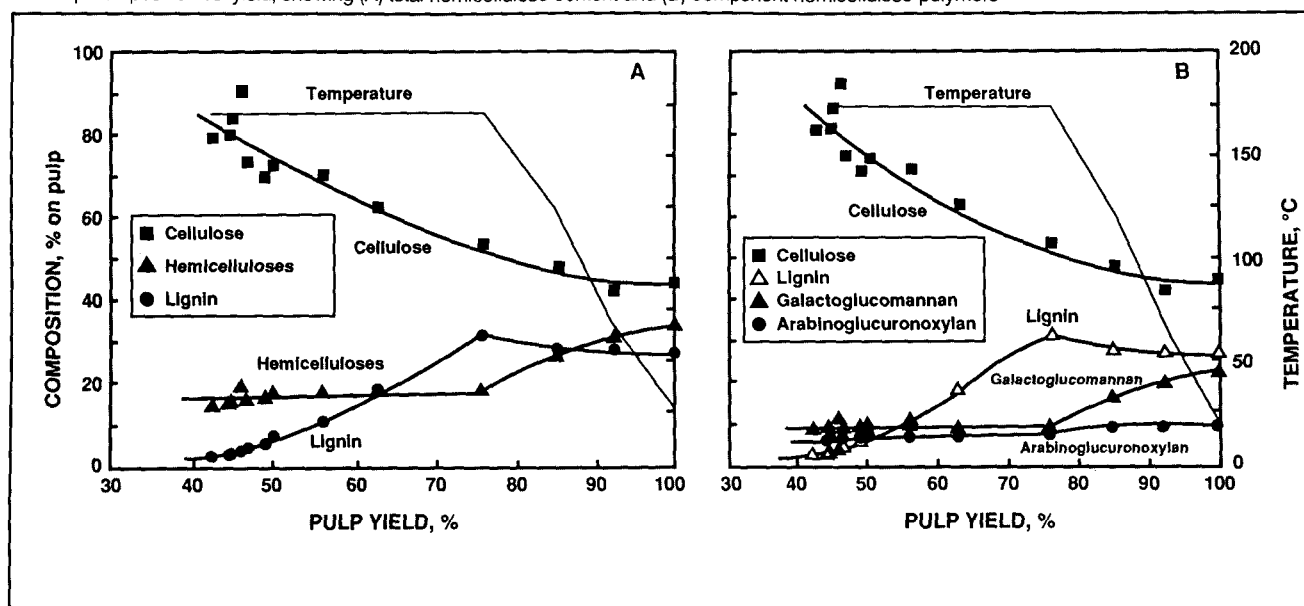
optimizing pulp viscosity. Their specific objective was, in fact, extended delignification without strength loss. The authors hypothesize selective delignification without carbohydrate degradation.

Several specific guidelines are established in their work. They recommend that the alkali concentration be leveled out over the duration of the cook, as opposed to an initial high concentration that gradually diminishes throughout the course of the cook. One can hypothesize that this step would minimize direct dissolution of carbohydrates. They also recommended that the concentration of HS^- ions be high. Presumably, this would result in diminished carbohydrate peeling reactions. They recommended that the ionic strength be maintained at a low level. Presumably, this would be best accomplished by maintaining low levels of lignin and sodium ions. This seems directed toward minimizing lignin condensation and carbohydrate reaction and solubility, particularly at the end of the cook.

Finally, they recommend low initial and final cook temperatures. This is consistent with earlier studies by Kondo and Sarkanen (9) showing higher carbohydrate losses with higher initial temperatures. It is also supported indirectly by Matthews's work (8), in which one could hypothesize high xylan loss at high temperatures in addition to the high mannan losses observed in the low-temperature stages of cooking. Sandstrom *et al.* (12) also recommend a low temperature at the end of the cook in an effort to minimize carbohydrate degradation.

Pulp optimization studies were reported recently by Greenwood (13), who described a modified continuous digester. Figure 2 shows the tear-tensile relationship for a northern softwood cooked to the same kappa number using a conventional kraft process. It also shows the relationship for the same wood cooked using modified continuous cooking to control the alkali charge as suggested by Sandstrom *et al.* (12). Although these data are not supported by carbohydrate analysis, it seems natural to attribute at least part of the improvement in the tear-tensile relationships to some preservation of carbohydrates.

4. Pulp composition vs. yield, showing (A) total hemicellulose content and (B) component hemicellulose polymers



Objective

Our objective was to determine cooking conditions that lead to maximum retention of hemicelluloses in kraft pulps. Pulps were cooked to a target kappa number using the conventional kraft process in a well-instrumented laboratory digester.

Discussion of results

The experimental procedures and statistical analyses are summarized under "Experimental procedures." Data are tabulated by Medhora (14) and Busayasakul (15). Details of the statistical analysis are given by Medhora (14).

Two sets of data were obtained in a laboratory digester. The first set (Data Set A) was used to follow the pulp yield, composition, and residual alkali through one complete time-temperature sequence at a fixed value of initial alkali, chip thickness, sulfidity, and liquor-to-wood ratio. A second set of pulping experiments (Data Set B) was conducted based on a central-composite, rotatable, second-order statistical design. Process variables studied were chip thickness, effective alkali, temperature, and cooking time at a fixed value for the sulfidity and liquor-to-wood ratio. Pulp composition was estimated from summative analysis techniques developed at the U.S. Forest Products laboratory by Effland and Harris (16). Time and

temperature were combined into the H-factor. Thus, independent process variables used to correlate pulp composition were:

- Chip thickness, mm, x_1
- Effective alkali, %, x_2
- H-factor, h, x_3 .

Response variables (Y) were kappa number, pulp yield, total hemicellulose, lignin, cellulose, galactoglucomannan, and arabinoglucuronoxylan contents.

Carbohydrate polymers

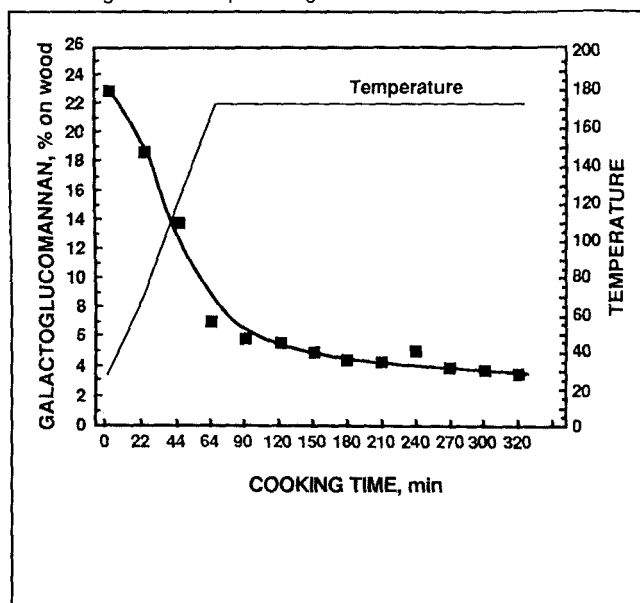
The experimental data for pulp yield, kappa number, extractives, and lignin content have already been published (17, 18). Figure 3 shows the experimental lignin and carbohydrate data plotted in the form of a Ross diagram. The lignin-to-carbohydrate composition ratio is plotted against pulp yield. Up to approximately 80% yield, little lignin is removed from the wood. Components being removed during this period are predominately extractives and hemicelluloses. Presumably, the hemicelluloses being removed are the lower molecular weight molecules of the distribution within the fiber (7). Again, at long times in the digesters, overcooking does not remove appreciable amounts of lignin, yet carbohydrates continue to be removed as the Ross diagram becomes flat.

Figures 4A and 4B present data

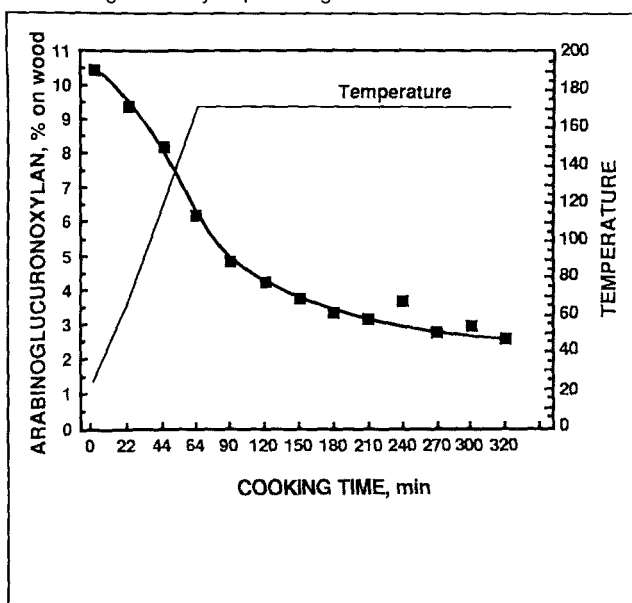
on the composition of the pulp for experiments that followed the time-temperature ramp (Data Set A). The major amount of hemicelluloses are lost during the heat-up period in the digester. Kondo and Sarkanen (9) showed substantial loss in hemicelluloses in the alkaline pulping of Western hemlock at temperatures as low as 80°C. Hamilton and Thompson (19) and Matthews (8) showed similar results for Western hemlock and slash pine, respectively.

Figures 5 and 6 show the amount of galactoglucomannan and arabinoglucuronoxylan removed during the pulping experiments, with both amounts given as percent on wood. On these graphs, the time-temperature ramp is superimposed to show when removal occurs from the pulp. In these experiments, the galactoglucomannan content decreased from about 22.9% in the wood at the beginning of the cook (25°C) to 7.04% on wood (9.31% on pulp) by the time the digester reached temperature, or the constant temperature portion of the cook. When the kappa number of the pulp reached 28.6 [Experiment A-9 by Busayasakul (15)], the final galactoglucomannan content was about 4.3% based on wood. At this point in the cook, the pulp yield was 46.6%, and the galactoglucomannan content was 9.26% in the pulp. On an absolute basis, this means that about 70% of the galactoglucomannan polymers were lost while the digester was being

5. Galactoglucomannan plotted against time



6. Arabinoglucuronoxylan plotted against time



II. Chemical lost (% on wood) during low and high parts of the kraft cook

	Lignin	Arabino-glucurono-xylan	Galacto-glucoman-nan	Cellu-lose
Amount in wood	26.9	10.4	22.9	44.4
Low temp. loss ^a	3.3	4.2	15.9	4.2
High temp. loss ^b	21.6	3.0	2.7	6.1

^aFrom the beginning of the cook to 170°C, reached after 64 min.
^bTime at temperature was 146 min. Kappa number was 28.6.

raised to temperature (Table II).

Likewise from Fig. 6, initially the wood contained about 10.4% arabinoglucuronoxylan. During the temperature ramp, 4.2% on wood of the xylan polymer had been lost, while another 3.0% on wood was lost during the constant temperature portion of the cook. Thus, in absolute terms, roughly 40% of the xylan losses occurred during the heat-up period of the cook. Table II contrasts the losses for lignin and cellulose during the heat-up and high-temperature periods. Our data (Table II) are in general agreement with those of Matthews (8) shown in Table I.

Contour plots

Contour plots were prepared by Medhora (14) for pulp yield, lignin content, and the carbohydrate composition of the pulp. Figures 7 and 8 show model values estimated from statistical equations given in "Experimental

procedures." The hemicellulose and galactoglucomannan contents are plotted against the effective alkali and H-factor. Similar results were also obtained for the arabinoglucuronoxylan polymer and total pulp yield.

Chip thickness was kept constant at 4 mm in Figs. 7 and 8. The contour plot shows that alkali decreases the hemicellulose polymers in the pulp at constant chip thickness. Alkali concentration has an important effect on the total hemicellulose content of the pulp (Fig. 7) and the galactoglucomannan polymers (Fig. 8). At constant H-factor, decreasing effective alkali charge leads to higher retention of the hemicellulose polymers in the pulp.

Figures 9 and 10 present additional contour plots predicted from the model equations. Here, contour diagrams were made as a function of chip thickness and H-factor. Similar results are available for arabinoglucuronoxylan and total yield (14). At

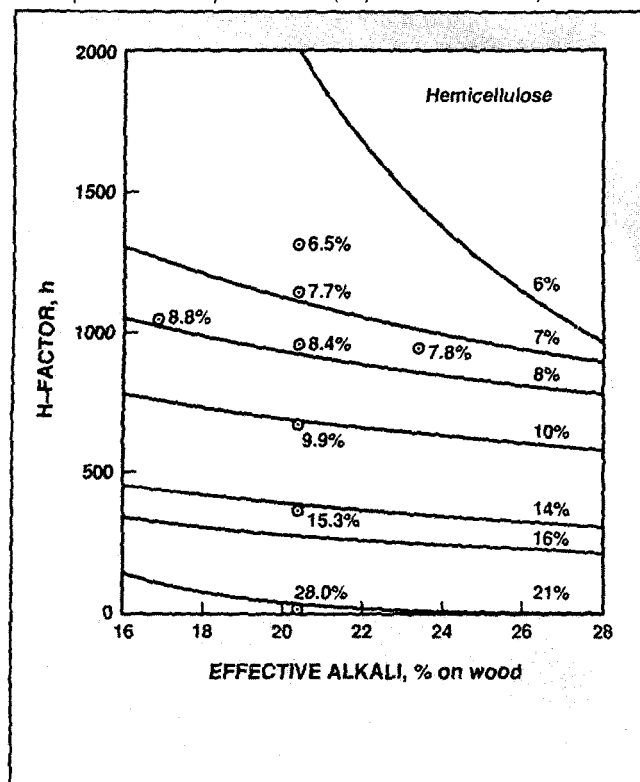
constant H-factor, increasing the chip thickness leads to an increase in the hemicellulose polymers (Fig. 9) retained in the pulp. This was true for both the galactoglucomannan (Fig. 10) and arabinoglucuronoxylan (not shown).

Please note that the contour lines in Figs. 7-10 are relatively flat. We believe this results from the high liquor-to-wood ratio (8.1:1) that Busayasakul used in his pulping experiments (15). High liquor-to-wood ratios cause the concentration of effective alkali to be low compared to cooks performed at conventional liquor-to-wood ratios (3-4 to 1). High liquor-to-wood ratios cause the composition of the hemicellulose polymers to be less sensitive to chip thickness and applied alkali. We would expect all of the curves (Figs. 7-10) to be steeper, had the experiments been performed at a more conventional liquor-to-wood ratio.

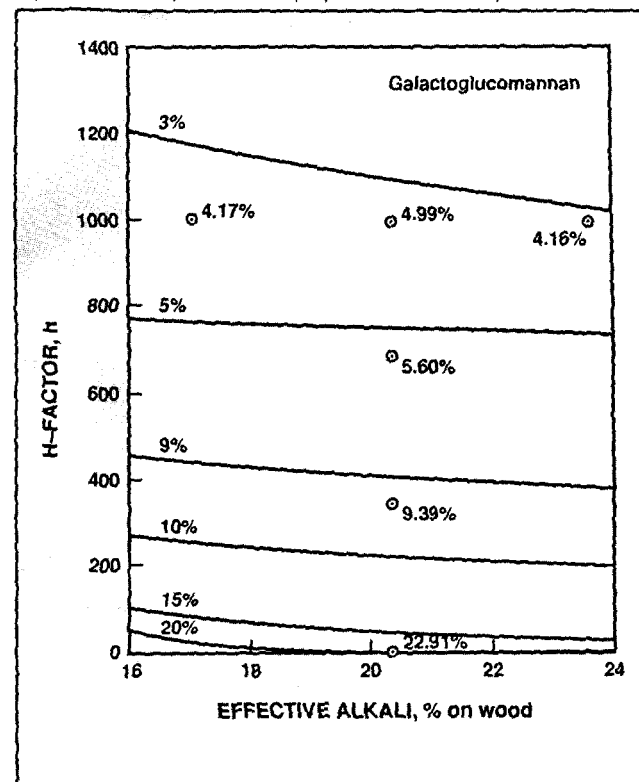
Optimum pulping conditions

In industrial practice, kraft cooking is always carried out to a target kappa number. Consequently, the regression equations were used to determine the effect that the kraft pulping variables have on changes in pulp composition and yield when the kappa number or lignin content is fixed at a target value. In the contour plots in Figs. 7-10, the lignin content of the pulp changes as the process variables change. Contour plots for the lignin

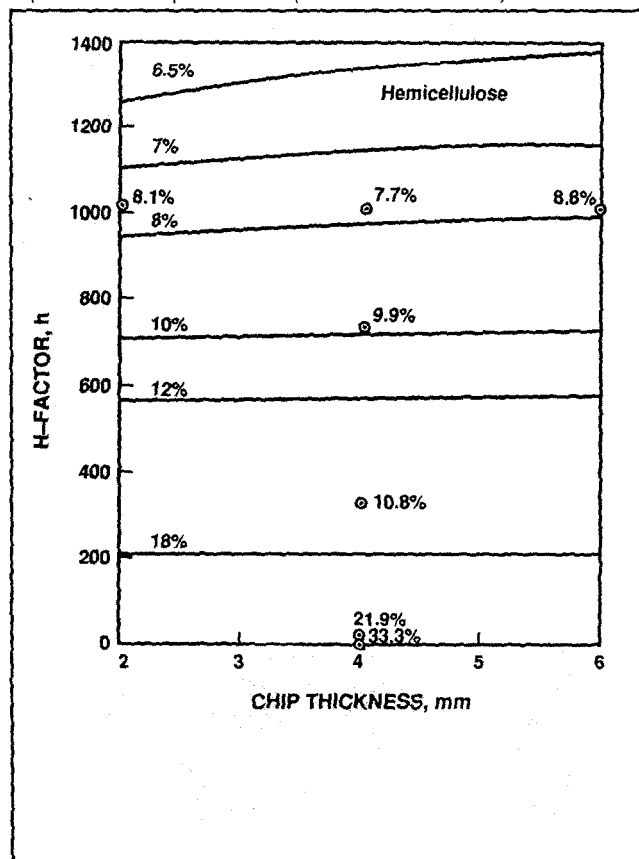
7. Total hemicellulose content vs. effective alkali applied and H-factor, with experimental data points circled (chip thickness = 4 mm)



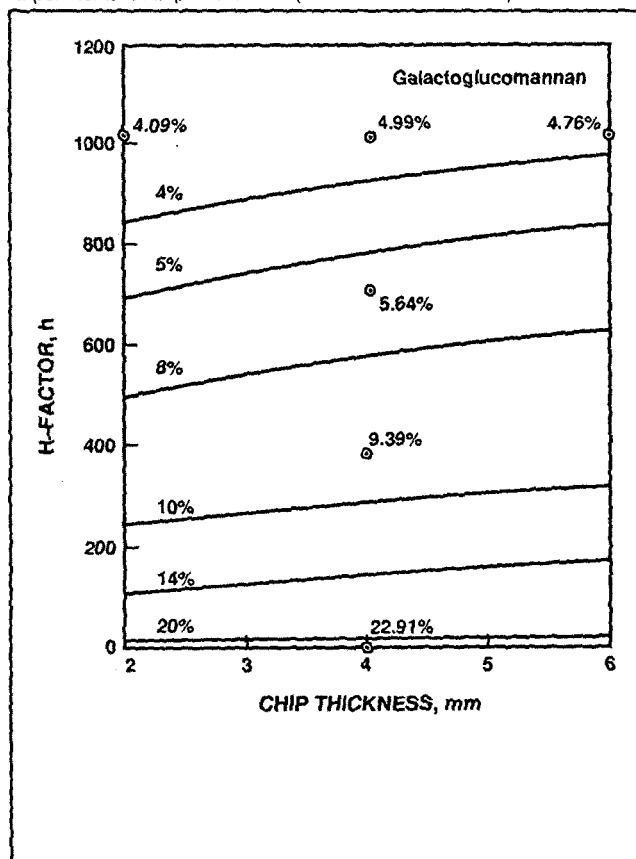
8. Galactoglucomannan content vs. effective alkali and H-factor, with experimental data points circled (chip thickness = 4 mm)



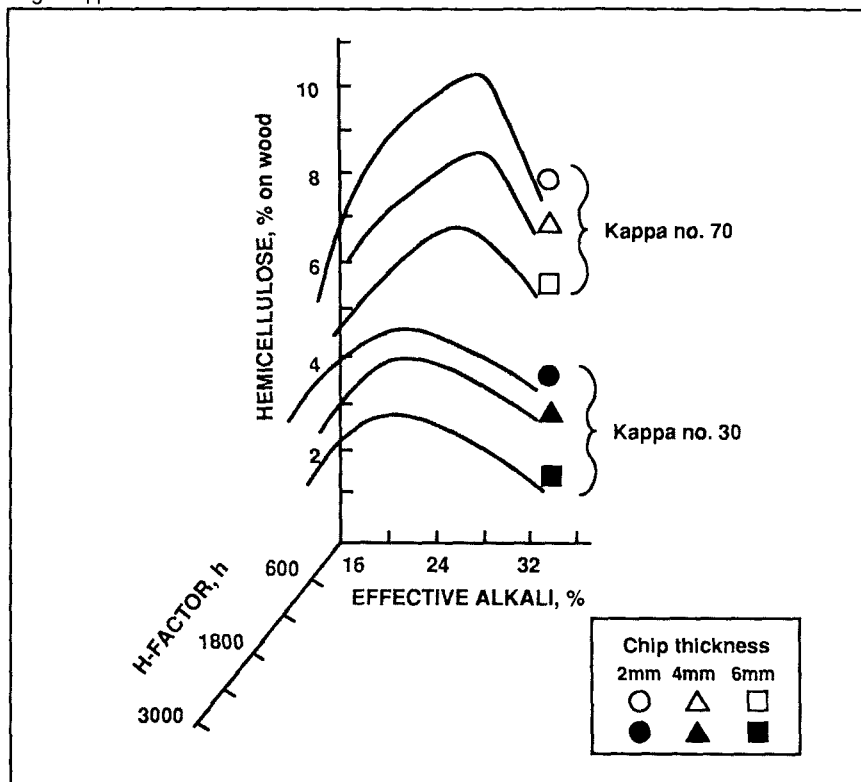
9. Total hemicellulose content vs. chip thickness and H-factor with experimental data points circled (effective alkali = 20.4%)



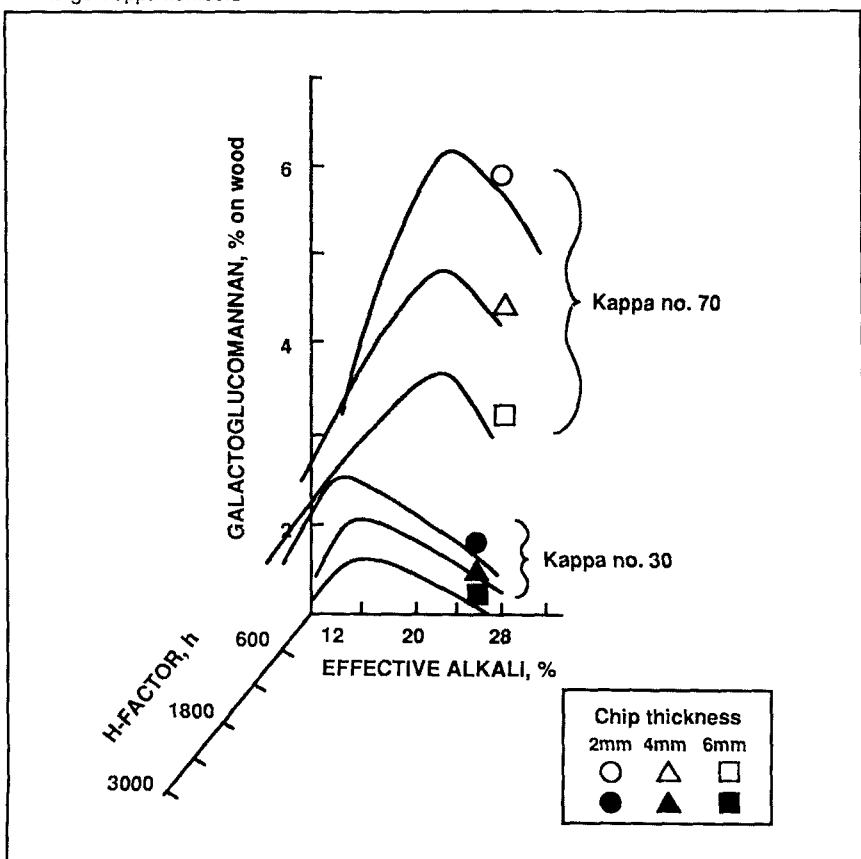
10. Galactoglucomannan content vs. H-factor and chip thickness, with experimental data points circled (effective alkali = 20.4%)



11. Total hemicelluloses retained vs. effective alkali and H-factor for different chip thicknesses and target kappa numbers



12. Galactoglucomannan retention vs. effective alkali and H-factor for different chip thicknesses and target kappa numbers



content in the pulp are given by Medhora (14).

Figures 11 and 12 are three-dimensional plots for the total hemicellulose and galactoglucomannan contents. Dependent variables are plotted against effective alkali and H-factor. Results are plotted for three different chip thicknesses (2, 4, and 6 mm) and at two different kappa numbers (30 and 70) in the pulp. Similar graphs were obtained for arabinoglucuronoxylan (not shown) by Medhora (14). Total pulp yield is shown in Fig. 13.

Figures 11-13 show that there are maxima in the three-dimensional graphs for yield, total hemicellulose, and component polymers. Figure 12 shows the results for galactoglucomannan, but similar results were obtained for arabinoglucuronoxylan also. These figures indicate that pulp yield, composition, and hemicellulose retention depend on process variables. For example, depending on process conditions, a variety of pulps may be produced with the same target lignin content. In all cases, decreasing the chip thickness increases the hemicelluloses retained in the pulp. This observation is consistent with the research work of Akhtaruzzaman and Virkola (20). These researchers also show that at a target kappa number, decreasing the chip thickness increased the breaking length and burst strength, which are dependent on the hemicellulose composition and the molecular weight of the hemicelluloses.

For any chip thickness used in the analysis, both the hemicellulose polymers in the pulp and the yield increased to a maximum and then decreased. This indicates that there are optimum cooking conditions for the effective alkali and H-factor that lead to maximum hemicellulose retention in the pulp. These results show the importance of cooking at optimum levels of effective alkali and H-factor to maximize pulp yield and composition. This observation was previously made by other researchers (7, 8).

Conclusions

Economic and quality advantages can be gained if a larger portion of the hemicellulose polymers can be retained during kraft cooking. Retention of hemicellulose depends in large

part on controlling process conditions and chip thickness. Arabinoglucuronoxylan and galactoglucomannans are removed largely during that period of the cook in which the wood is being raised to the cooking temperature. Arabinoglucuronoxylan is more stable than the galactoglucomannan polymers and is removed later during the period in which the temperature is rising.

A higher alkali charge results in lower hemicellulose retention and yield when cooking to a constant H-factor at fixed chip thickness. At fixed alkali charge, less hemicellulose is retained when cooking to higher H-factors with small amounts of lignin removed. There are maximum values in the pulp yield and hemicellulose composition curves when pulping to a fixed or target kappa number. Thinner chips lead to higher hemicellulose retention values. Cooking conditions must be carefully controlled to retain hemicellulose more effectively and improve brownstock pulp quality.

Experimental procedures

Kraft cooking

Busayasakul performed the kraft cooking of red spruce (*Picea rubens sarg*). Wood samples that were free of compression wood were selected. Forty-three cooks were performed, giving two sets of data. In the first series of experiments (Data Set A), the pulp yield and composition were followed through one complete time-temperature sequence at a fixed value of the initial alkali, chip thickness, sulfidity, and liquor-to-wood ratio. Pulping conditions were:

Wood: 25 g (moisture-free basis)

Chip size: 15.9 mm × 15.9 mm × 4 mm thick

Active alkali: 24%

Sulfidity: 30%

Liquor-to-wood ratio: 8.1 to 1

Time to temperature: linear ramp of 64 min

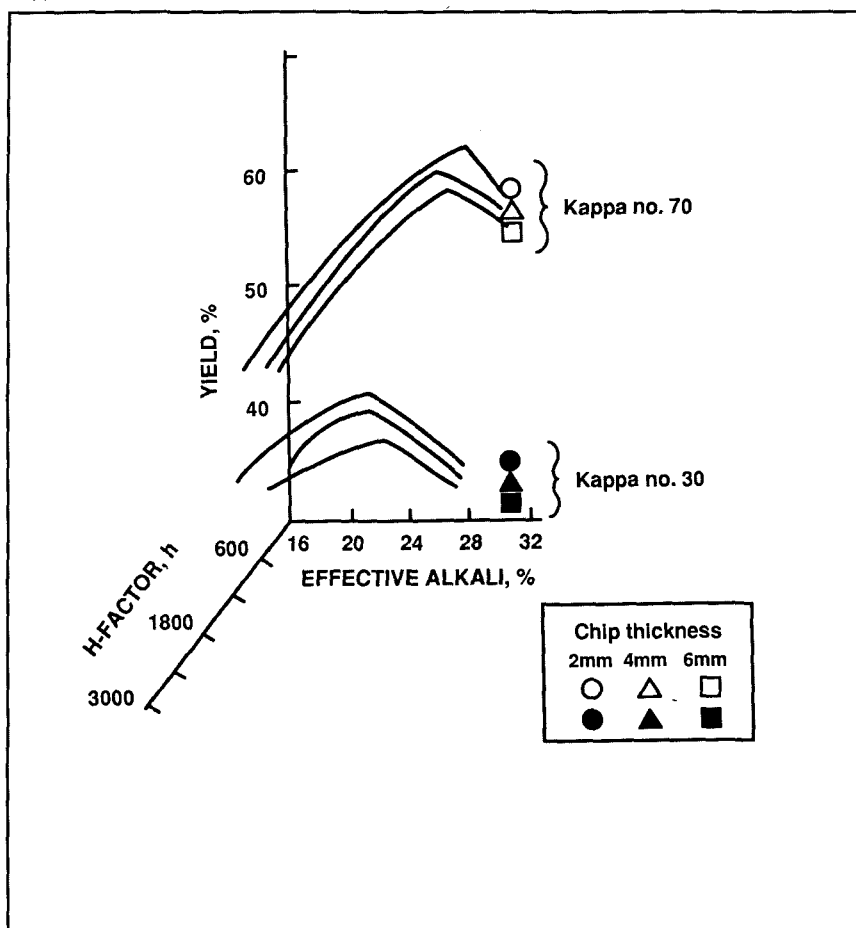
Cooking temperature: 170°C

Time at temperature: variable, depending on the sample (0 to 150 min).

Thirteen pulps of different yield and composition were produced in these experiments.

A second set of pulping experiments (Data set B) was conducted randomly

13. Total pulp yield versus H-factor and effective alkali for different chip thicknesses and target kappa numbers



based on a central composite, rotatable, second-order statistical design. Process variables were chip thickness, active alkali, temperature, and cooking time at a fixed sulfidity and liquor-to-wood ratio. Altogether, 31 pulps were produced using the central composite, rotatable, second-order experimental design. The advantage of a statistical design is that polynomial regression equations are easily fit to the experimental data. Sulfidity was kept constant at 30%. The ranges for the four variables examined by Busayasakul are as given in Table III.

Pulp composition

The polymeric composition of the samples was determined using summative analyses methods developed at the U. S. Forest Products Laboratory (16). This technique is shown schematically in Fig. 14. The sample was broken down into four categories of wood components:

1. Extractives (E)

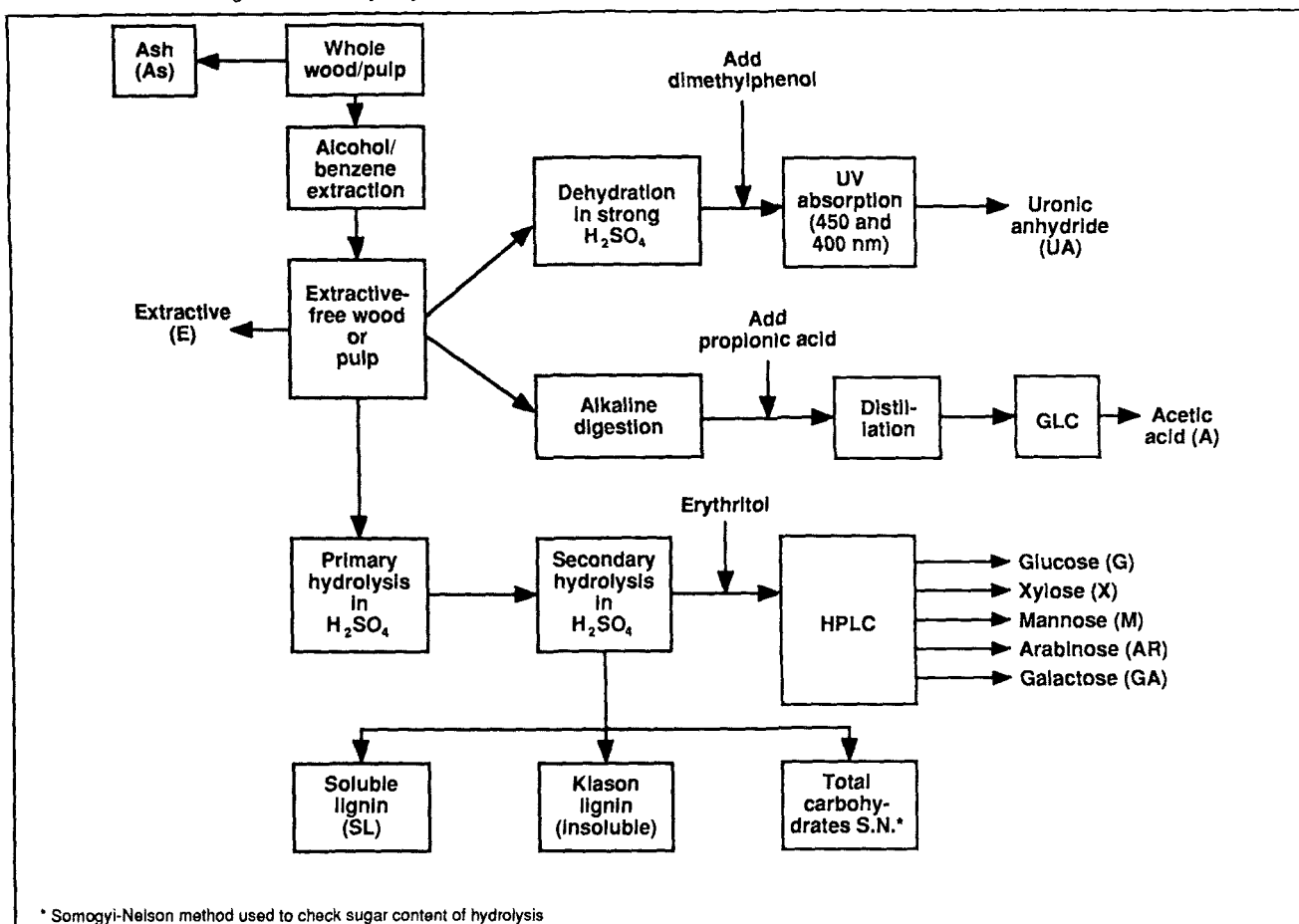
III. Ranges for the four pulping variables

Chip thickness, mm	2-6
Active alkali, %	20-28
Temperature, °C	160-180
Time, min	90-210

- Ash (As)
- Total lignin (TL)
Insoluble or Klason type (KL)
Soluble Lignin (SL)
- Total Carbohydrates (TC)
Acetyl groups (A)
Glucose (G)
Xylose (X)
Galactose (GA)
Arabinose (AR)
Mannose (M)
Uronic anhydride (UA).

Medhora (14) used Busayasakul's data to estimate the galactoglucomannan and arabinoglucuronoxylan contents of the pulp and wood samples.

14. A diagram of procedure for analyzing the wood and pulp. The major groups are the extractives, carbohydrates, and lignin*. Somogyi-Nelson Method used to check sugar content of hydrolysis.



IV. Equations used in estimating the polymeric composition of the samples

Total lignin	=	KL + SL	(1)
4-O-methylglucuronic anhydride	=	UA (190/176)	(2)
% glucan	=	G (162/180)	(3)
% mannan	=	M (162/180)	(4)
% arabinan	=	AR (132/150)	(5)
% galactan	=	GA (162/180)	(6)
% xylan	=	X (132/150) + UA ((132 × 0.6)/176)	(7)
Total carbohydrates	=	% glucan + % xylan + % arabinan + % galactan + % acetyl + % 4-O-methylglucuronic anhydride	(8)
% Cellulose	=	Glucan - $\left(\text{mannan} \times \frac{1 \text{ mole glucose}}{3.5 \text{ mole mannose}} \right)$	(9)
% hemicelluloses	=	% total carbohydrate - % cellulose	(10)
Galactoglucomannan (% on pulp)	=	mannan + galactan + glucan + acetyl groups	(11)
Arabinoglucuronoxylan	=	xylan + 4-O-Me- α -D-glucuronic anhydride + arabinan	(12)

Based on 100g of sample.

Ash and extractives. Ash in the wood was determined using TAPPI Test Methods T 15 and T 211. The wood was extracted with alcohol and benzene using TAPPI Test Methods T 6 and T 204.

Lignin. Acid-insoluble or Klason lignin (72% H₂SO₄) was determined gravimetrically using the method of Effland (21), which is a modification of TAPPI Test Method T 222. Carbohydrates were removed from the samples by primary and secondary hydrolysis with concentrated H₂SO₄. Acid-soluble lignin was determined spectrophotometrically by measuring the transmittance of undiluted hydrolyzate at 205 nm (TAPPI um 250).

Acetyl groups. Acetyl groups were determined using the method of Browning (22). Gas chromatographic measurements were performed to determine acetic acid after NaOH hydrolysis. Propionic acid was used as the standard.

Uronic anhydride. Measurements were determined using chromophoric

V. Summary of regression constants for response variables

	Kappa number	Yield, %	Hemi-cellulose, % on wood	Lignin, % on wood	Cellulose, % wood	Galacto-glucoman, % on wood	Arbino-glucoronyl, % on wood
r^2	0.93	0.92	0.75	0.94	0.82	0.70	0.86
b_0	394.412	77.714	19.0338	32.9958	39.87722	10.5618	7.87404
b_1	5.9767	1.232	0.08426	0.6476	0.50202	5.822×10^{-2}	2.432×10^{-2}
b_2	-20.903	0.218	0.4563	-0.6756	0.04756	0.38174	0.12993
b_3	-0.118	-0.039	-0.02601	-0.03002	-6.52×10^{-3}	-1.901×10^{-2}	-7.09×10^{-3}
b_4	0.383	-0.0216	-0.01425	+0.00428	-4.274×10^{-3}	-9.74×10^{-3}	-5.661×10^{-3}
b_5	3.638×10^{-5}	1.603×10^{-5}	1.295×10^{-5}	1.321×10^{-5}	3.1232×10^{-6}	9.830×10^{-6}	3.1946×10^{-6}
b_6	3.81×10^{-9}	-2.108×10^{-9}	-1.887×10^{-9}	-1.7881×10^{-9}	-4.8116×10^{-10}	-1.4527×10^{-9}	-4.4882×10^{-10}

groups analysis according to the method of Scott (23). Samples were dehydrated with sulfuric acid, and UV absorption measurements were made at 450 and 400 nm. Dimethylphenol was used as a standard.

Sugar analysis. Component sugars, glucose, xylose, mannose, arabinose, and galactose were determined from HPLC measurements made on the samples following secondary hydrolysis. (HPLC stands for "high-performance liquid chromatography.") The method of Paice *et al.* (24) was used with erythritol as the standard. The total amount of carbohydrates found in the sample from the HPLC analysis was checked using the Somogyi-Nelson method (TAPPI Test Method T 250) for total carbohydrate analysis.

The wood polymers were estimated from the pulp composition using equations developed by Effland and Harris (16) at the U. S. Forest Products Laboratory. The FPL method is similar to that given by Hamilton and Thompson (19). Equations are summarized in Table IV, and details are given by Busayasakul (15).

Xylan polymer. An additional factor was considered in estimating the xylan fraction of the carbohydrates. The 4-O-methylglucuronoxylan is glycosidically linked to xylan through the No. 2 position on the xylose units. This particular bond is quite resistant to hydrolysis—much more so than the other glycosidic bonds present.

The U. S. Forest Products Laboratory estimates that 60% of these linkages survive the primary and secondary hydrolysis steps (16). Thus, if you begin with one mole of 4-O-methylglucuronic anhydride bound to

the xylan in the sample, then after hydrolysis, 0.6 moles will still be linked to xylose units. The unhydrolyzed xylose is present as a dimer (biouronic acid) consisting of the 4-O-methylglucuronic anhydride unit linked to a xylose unit. The remaining 40% of the xylose units have been hydrolyzed away.

The free 4-O-methylglucuronic acid as well as the biouronic acid units are virtually all picked up by the chromophoric group analysis used in determining glucuronic anhydrides. But the xylose sugar determined from the HPLC analysis will be low since the HPLC does not detect biouronic acid. Consequently, the total unhydrolyzed xylose (xylan polymer) in the samples was estimated by Eq. 7 (Table IV) using an appropriate correction factor.

Carbohydrate polymers. An estimate was made for the hemicellulose and cellulose polymers for the carbohydrate portion of the pulp. We did this by assuming that the glucan was found predominantly in the cellulose polymer except for a small amount associated with the (galacto)-glucoman polymers—that is, no other hemicelluloses contain glucose. In making an estimate in this manner, we must assume that there is a glucose-to-mannose ratio for the glucose found in the glucoman and galactoglucoman polymers. For this work, we assumed that the glucose-to-mannose ratio was 1 mole to 3.5 moles for softwood glucoman and galactoglucoman. This ratio is suggested by Rydholm (25) and is in agreement with the data presented by Sjostrom (26).

Thus, the cellulose and hemicellulose fractions of the samples were

obtained from Eqs. 9–10. The combined galactoglucoman and (galacto)-glucoman polymers were estimated together from the mannan, galactan, acetyl, and that portion of the glucan polymers not associated with cellulose (Eq. 11). The arabinoglucuronoxylan polymer was estimated as the xylan, 4-O-Me- α -D glucuronic anhydride and arabinan fractions of the pulp (Eq. 12).

Statistical analysis on pulp components

Time and temperature were combined into one variable, H-factor, by using Vroom's method (27):

$$H = \int_0^t k(T) dt \quad (13)$$

where

k = Vroom's relative rate constant (unitless)

T = temperature, °K

t = time, h.

and

$$k = \ln^{-1} (43.20 - 16,113/T) \quad (14)$$

Consequently, the input variables used in the statistical analysis were chip thickness, effective alkali, and H-factor.

The data from Busayasakul's 44 experiments were analyzed to provide regression equations of the general form which includes third order and interaction terms:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^n b_{iii} x_i^3 + \sum_{i,j=1}^n b_{ij} x_i x_j \quad (15)$$

where

Y = response variable

x_1 = chip thickness, mm

x_2 = effective alkali, %

x_3 = H-factor, h.

and $b_0, b_i, b_{ii}, b_{iii}, b_{ij}$ are empirical constants for the model. Response variables were pulp kappa number, yield, total hemicellulose content, lignin, cellulose, galactoglucomannan, and arabinoglucuronoxylan.

Statistical analyses were performed using the "Statistical Analysis Systems" (SAS) (28) computer program available at the University of Maine. The PROC REG subroutine was used to perform three-variable regression analysis having the form shown in Eq. 15. The objective of this analysis was to determine statistical models that gave the best fit of the pulp composition data as determined by the coefficient of multiple determination. An ideal fit of the model to the data would have a coefficient of determination equal to 1, while no correlations would be equal to zero.

The statistical model that best fit the pulp composition data for the response variables was:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_2^2 + b_5x_3^2 + b_6x_3^3 \quad (16)$$

Table V lists the values of the statistical coefficients (b_i) and the coefficient of determination (r^2) for the model fit to the composition data. The r^2 values ranged from a low of 0.70 for galactoglucomannan to a value of 0.94 for the lignin content.

Please note that composition data were correlated as percent on wood, which is a method often found in related literature. To convert the pulp composition data from percent on pulp to percent on wood, one must know pulp yield:

$$\% \text{ on wood} = (\% \text{ on pulp}) \times (\text{yield, \%})/100 \quad (17)\square$$

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