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THE KINETICS OF PULPING ASPEN WOOD
WITH SODIUM SULFITE SOLUTIONS

By

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SUMMARY

The object of this investigation was to determine the most favorable conditions of pulping aspen wood with solutions of sodium sulfite to obtain yields above 70 percent. The rates of removal of pentosans (the easily-removed fraction of the carbohydrate content of wood) and lignin were measured in order to determine the conditions favoring a minimum pentosan loss and a maximum lignin removal.

It was found that a critical yield exists for each temperature. The critical yield is defined as the yield at which the rate of lignin removal just equals the rate of pentosan removal. For a given temperature, therefore, it is advantageous to use cooking times which would result in pulp yields slightly less than the critical yield.

The effect of sodium sulfite concentration was examined. For the removal of pentosans, the liquor concentration shows an optimum value of 65 to 75 grams per liter at which there is a minimum loss of pentosans. For the combined requirement of a minimum pentosan loss and a maximum lignin removal, concentrations of less than 50 grams sodium sulfite per liter are unfavorable.

It was also found that the rate curves for lignin and pentosan removal (logarithmic rates plotted against reciprocal absolute temperatures) showed a sharp rise at high temperatures, indicating the possibility that the over-all availability of these wood fractions undergoes a change at high temperatures. This is attributed to structural changes in wood.

The mechanism of the complex pulping reactions may be explained by considering the over-all pulping reaction to be composed essentially of two general reactions, namely,

1. Removal of lignin
2. Removal of carbohydrates

Rates of each of these reactions can be expressed in terms of the instantaneous amount of that particular fraction and its availability. The availability of each fraction is dependent on the instantaneous total pulp content. On this basis, two independent rate equations have been derived for the removal of lignin and carbohydrates. The sum of these separate rates is the total rate of pulping. The mechanical correlation of data has been restricted tentatively to temperatures of 200°, 210°, and 220° C., and for yields above 70 percent. The agreement between the calculated and experimental rates and amounts of lignin, carbohydrate and total wood substance (yield) removal has been found to be within ± 5 percent.

The rate equations obtained are given below:

For lignin removal

$$r_1 = (1.1)\,(10^6)\,(e^{-\frac{15,300}{RT}})\left[1 - \alpha_1(x_1 + x_2)\right]x_1$$

For carbohydrate removal

$$r_2 = (2.42)\,(10^6)\,(e^{-\frac{15,800}{RT}})\left[1 - \alpha_2(x_1 + x_2)\right]x_2$$

Total yield

$$r = r_1 + r_2$$

where

r_1 = rate of lignin removal (grams per gram of wood per minute)

r_2 = rate of carbohydrate removal (grams per gram of wood per minute).

x_1 and x_2 are the instantaneous amounts of lignin and carbohydrates present, respectively.

α_1 and α_2 are constants depending on the nature of the wood.

For aspen wood,

$\alpha_1 = 2.49$

$\alpha_2 = 1.54$

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CHAPTER I

REASONS FOR INVESTIGATION

The object of this investigation was to increase knowledge concerning the mechanism of pulping wood with sodium sulfite solutions in producing a product of pulp in yields above 70 percent. There presently exists little fundamental information on the high-yield sodium sulfite pulping process which has recently become established as one of the major pulping methods of the wood pulp industry. The importance of this process in the potential conservation of forest resources and the utilization of all available species of woods, particularly the hardwoods, has also become well recognized. With the introduction of semichemical pulping, the use of sodium sulfite liquors has been greatly increased.

The study of the mechanism of the pulping of wood by any process is complicated because the actual constitutions of the two major fractions of the wood that influence the quality and the quantity of the pulps derived therefrom are to a great extent unknown; these fractions are the hemicelluloses associated with cellulose for the most part in the cell walls of the wood fibers, and the intercellular material which is predominantly lignin. Many formulae have been postulated for the lignin molecule, but there are strong reasons to believe that the lignin, as it occurs in wood, differs in constitution from the isolated lignin. In addition to the heterogeneity of the wood itself, each of the reactions involved in pulping is heterogeneous. This makes the study of the pulping reaction kinetics extremely complicated. The commonly used pulping agents heretofore have been calcium bisulfite in sulfurous acid for sulfite pulping, sodium hydroxide for soda pulping, and a mixture of sodium hydroxide and sodium sulfide for sulfate pulping. Of these, the sulfite process has received the most attention in kinetic studies. Most theories have been restricted to the delignification reaction with little speculation on the theories of hemicellulose removal. It is known, nevertheless, that during the early part of sulfite pulping the rate of removal of certain carbohydrates, mostly hemicelluloses, exceeds the rate of lignin removal because of the more easily hydrolyzable nature of these carbohydrates. It is also known that the rate of loss of carbohydrates is decreased relative to the rate of lignin removal in the later stages of the pulping reaction. It is apparent, therefore, that it is difficult to retain the much desired carbohydrates and at the same time to remove the unwanted lignin. In this respect, the results from the soda and the sulfate processes follow the same trend. On the other hand, it is possible to control to some extent the relative amounts of lignin and hemicelluloses removed, and their relative rates of removal, by using pulping reagents and procedures other than those commonly employed in the past.

CHAPTER II

PREVIOUS INVESTIGATIONS AND LITERATURE REVIEW

Cross in 1880 (9) was the first to suggest the use of sodium monosulfite for pulping wood. He proposed that the so-called lignocellulose was hydrolyzed by the sodium sulfite and that the reactive aldehydic and acidic groups of the lignin molecule were fixed by the sulfite and the basic groups, respectively, of the pulping liquor. Since the work of Cross the field remained almost unexplored until about 1920, when a significant commercial application was proposed by Bradley and McKeefe (6) for using sodium sulfite. Brot and Hirschell (8) determined the effect of sodium sulfite concentration on the over-all yield of pulp. In cooking cereal straw, they found that the yield of pulp at first decreased with increasing sodium sulfite concentration, reaching a minimum at a concentration of 4 percent. Above 4 percent the yield increased progressively. It was proposed that the rise in yield with concentrations above 4 percent was due to the inhibition of the erosive action of the liquor on the fiber, the excess sodium sulfite suppressing hydrolysis. Later studies by Rawlings and Staidl (15) were of a more comprehensive nature. They reported that the concentration of the sulfite had little effect, if any, on the removal of the various constituents of wood. Their data indicated that the complete removal of lignin would require temperatures at which the total yield of pulp would be less than 50 percent. Little nonlignin material was removed below 170° C., and it was suggested that 140° C. would be the best temperature for obtaining high yields, since at that temperature, though delignification would be incomplete, little cellulose would be destroyed.

From the data of Brunn on alkaline pulping, Arrhenius (4) suggested that the pulping of wood follows a first order rate equation. His "rate constant" was not constant over the range of conditions investigated.

Bray and Eastwood (5) have reported some interesting conclusions about delignification. Their experiments covered yields ranging from 85 to 60 percent, and temperatures of 140°, 150°, 160°, and 170° C. Using a 25-gram sample of wood and a sodium sulfite concentration of 50 grams per liter, they digested for periods ranging from 1 to 8 hours. Assuming the yield to decrease according to a modified first order equation, from the observation that the first order "rate constant" decreased with decreasing yield according to a certain pattern, they developed empirical equations for predicting the yield for a given time and temperature. For the delignification reaction, these workers assumed that one of the reactants, in this case the pulping chemical, remains constant as the reaction proceeds. This may be justified by the fact that the reagent molecules, being of small size, far outnumber the lignin molecules which are originally in a high state of polymerization. On this basis and on experimental evidence, a second order equation was proposed for delignification and another empirical equation derived.

Aronovsky and Gortner (3) studied the effect of sodium sulfite concentrations and temperatures on the rates of destruction of cellulose, pentosans, lignin and total wood substance. Using aspen sawdust and temperatures of 170° and 186° C., they made the following observations:

a. The original lignin was progressively destroyed as the salt-wood ratio was increased from zero to 0.238. Doubling this ratio resulted in a slight but definite increase in lignin removal. Lignin removal, according to them, proceeds in two stages, namely by depolymerization followed by reaction between sodium sulfite and the products of depolymerization.

b. Pentosan removal was much less drastic than with either pure water, sodium sulfate, or sodium thiosulfate. Doubling the sulfite concentration, however, increased the rate of pentosan destruction, contrary to the effect in the low concentration range.

c. The destruction of cellulose was remarkably low, a situation most desirable for high-yield pulping.

Choice of Liquor

The use of water alone as a pulping reagent has limited application in semichemical pulping for high yields because the organic acids formed with the acid-forming groups in the wood remove little of the generally unwanted lignin and tend to destroy the pentosans and other carbohydrates instead (1). Since the hydrolysis of cellulose occurs by cooking wood in the presence of free acids and alkalies, the cooking should be done in a neutral medium to minimize the loss of cellulose. It is known that organic acids are released from wood during cooking so that a salt that would preserve a neutral or near-neutral state should be added. Sodium sulfite, being a salt of a weakly dissociated polybasic acid, exerts such a buffering action when used in excess. Of the many possible salts belonging to this category, sodium sulfite has been most used because of its relation to the soda process through the sodium ion on the one hand, and to the sulfite process through the sulfite ion on the other. Aronovsky and Gortner (2) have studied the effect of adding various salts on the rates of removal of lignin and pentosans. Their specific data on sodium sulfite pulping indicate the advantages of using this chemical (3). A further advantage is the fact that the semichemical process removes sufficient lignin to soften the chips and thus permits defibration by mechanical means into pulp composed substantially of individual fibers with paper-making qualities.

CHAPTER III

EXPERIMENTAL METHODS

The experimental technique employed in this investigation was divided into two parts. The work up to 190° C. was carried out in glass tubes placed in a pressure autoclave, referred to here as the steam digester. Above 190° C., a salt bath was used and stainless steel reactors were substituted for the glass tubes.

The Pressure Autoclave

A photograph of the pressure autoclave is shown in plate 1. This is the same autoclave as employed by Saeman in his wood hydrolysis experiments (16). The sealed glass tubes were tied to a copper rack that fits into the digester. The rack, together with the lid of the digester, was operated by a pulley and chain. The use of test tubes for small-size samples is advantageous in that many samples with different liquor concentrations and wood-liquor ratios can be easily cooked simultaneously under identical conditions for a given time and temperature. The collection of many simultaneous samples makes the data at different temperatures and different times of digestion much more comparable. In conducting a digestion, air was first driven out of the autoclave by operating the flush valves after which these valves were closed and the steam introduced until a pressure was built up in the digester corresponding to the required temperature, as indicated by the pressure gage. The valve which regulates the steam inlet maintains the temperature inside the digester constant to within 0.5° C.

The actual period of digestion was taken as that between the instant the pressure gage registered the desired pressure and the instant the steam blow-off was started. This requires consideration of the effect of the initial heating period in reaching the desired temperature of operation, and also the time required to reduce the steam pressure to atmospheric at the end of the run. A typical case may be considered, say 170° C. It is known that the pulping reaction rate is approximately doubled for each 10° C. rise in temperature. The normal heating and the blow-off periods are of the order of 1 minute each. The average temperature during the heating up to 170° C. is 140° C. The equivalent time at 170° C., therefore, would be one-fourth minute. Since this one-fourth minute appears in each run of the digester, its only effect, if neglected, would be to displace the time-yield curves along the time axis uniformly for all the runs at that temperature. The average temperature during the heating period for the other final temperatures investigated, namely 150° C. and 190° C., were 130° and 155° C., respectively. It is apparent that the equivalent time for the heating period for each of the temperatures is one-fourth minute or less. The rate of steam blow-off is so adjusted that the equivalent time for the blow-off period for each of the temperatures is also one-fourth minute. Thus for each run a total of one-half minute must be added to the "cooking time" as defined earlier.

The Molten Salt Bath

For temperatures of 200° C. and above, a molten mixture of the nitrates of sodium, potassium and lithium was used in the constant temperature bath. This bath was contained in an asbestos-covered container (plate 2) heated electrically by eight resistances in series. Large temperature adjustments were made by switching off one or more of the resistances as required. The salt bath was kept well stirred during the entire period of cooking. The final temperature was maintained constant by a thermal regulator to ± 0.1° C. Data on the properties of this salt mixture are available in the International Critical Tables (11). One of the advantages in using a salt bath is the fact that any salt adhering to the reactors can be easily removed by cooling and washing in cold water.

Reactors

The pulping reactions proceed very fast in the initial stages of cooking. In a batch reaction of this type, a small rise in temperature may result in a lowering of the reaction time from several hours to a few seconds. To secure temperature control, therefore, the reactors used for such rapid reactions must have:

a. high heat conductivity
b. adequate strength
c. low heat capacity
d. corrosion resistance

Details concerning such reactors with various metals of construction have been studied by Saeman and others (17). The reactors used in this present investigation were designed on the same lines (plate 3). Data on the reactors are given below.

Material: all parts coming in contact with the liquor of stainless steel; the rest of monel.

Length: 10 inches.

Diameter: 3/8 inch.

Volume: 4.43 cubic inches.

Stainless steel was chosen because (17) of its ability to withstand high internal pressures almost independent of temperature.

The reactors were suspended in the bath by the long-handle holder shown in plate 2.

Equivalent Time Calculations

From a knowledge of the temperature coefficient of the pulping reactions, it is known that at 200° C. or above, less than 20 minutes would be required for a yield of 70 percent. At these high temperatures for such short periods of cooking, the heating and the cooling periods have a significant effect and must, therefore, be properly accounted for.

The rate of heating of the reactors was estimated by measuring the time required for a thermocouple to reach various temperatures. This was done by welding the end of a copper-constantan thermocouple into the end of a 1/8-inch copper tubing. This end was placed in the reactor. The measured rate of temperature rise is less than the true rise due to the lag introduced by the thermocouple well and the measuring instrument.

Figure 1 shows the experimental curve obtained for a bath temperature of 200° C. Since the curves for the higher temperatures almost coincided with this curve, they are not shown separately. ΔT denotes the temperature difference between the bath and the reactor at any given instant of time. It is seen that 57 seconds are required for the reactor to reach 199.5° C. (for a bath temperature of 200° C.). In table 1 are given the values of the first order reaction rate constants for a few selected values of the reactor temperature. The rate constants at 150°, 170°, 190°, 200°, 210° and 220° C. were obtained experimentally by assuming the over-all pulping reaction to be unimolecular. For the intermediate values of the temperature (e.g., 195° C.), the velocity constants were calculated from the Arrhenius equation using an activation energy of 27,000 calories per gram mole, since this value represents the average value for the pulping reactions in the high yield range. A sample calculation of the equivalent time at 200° C. is shown below.

Table 1.--Time-temperature Relation for the Heating Period and the Corresponding Reaction Velocity Constants

Temperature inside reactor (T)	$\triangle T$ for a bath temperature of 200° C.	Time (t)	Velocity constant (k)
°C.	°C.	Seconds	(Min.) 10^3
150	50	19	0.2637
170	30	23	0.785
190	10	34	2.88
195	5	38	4.3
199.5	0.5	57	5.56

Plots of the velocity constants against time are shown for final temperatures of 200° C., 210° C., and 220° C. (fig. 2).

The area kt of the curve for t = 57 is 0.0023.

Assuming that the rate is given by the first order equation

$$- \frac{dx}{dt} = kx \text{ ---------------- } (1)$$

where x = percent of original remaining in the wood we get, on integration

$$- \log x = \frac{kt}{2.303} \text{ ----------- } (2)$$

$$\log x = - \frac{0.0023}{2.303}$$

$$x = 99.8\%$$

Hence, amount converted = 0.2%.

Now, at 200° C., k = 0.00581.

Therefore, from equation (2),

$x = 90.75\%$ for 1000 seconds (arbitrarily taken).

The amount converted if the reaction were to proceed uniformly at 200° C. without a heating period would be 9.25 percent. Hence, equivalent time (defined as the time equivalent at the final temperature corresponding to the total reaction during the heating period)

$$= \frac{0.2}{9.25}(1000)$$

$$= 22 \text{ seconds.}$$

Similar calculations were made for 210° C. and 220° C. and the results are tabulated in table 2.

Table 2.--Equivalent Times for the Heating Period

Temperature	Equivalent time
°C.	Seconds
200	22
210	25
220	27

These values are shown graphically in figure 3.

Analytical Procedure

The size of the wood samples taken for analysis was 0.6 gram where the steam digester was used and 0.3 gram when the salt bath was employed. This reduction in sample size was necessary because a smaller reactor was used in the salt bath. The glass tubes were sealed after introducing the wood meal and liquor and cooked in the steam digester. After digestion the tubes were broken by an electric cutter and the contents washed into weighed Gooch crucibles with carbon dioxide-free distilled water. The residual pulps were dried overnight at 105° C. and analyzed as follows.

1. Carbohydrate material: This was analyzed in terms of potential reducing sugar after hydrolysis of the pulp with 72 percent sulfuric acid according to the technique developed by Saeman (18). The analysis of the sugars followed the method of Shaffer and Somogyi (19).

2. Pentoses and pentosans: The sugars obtained by the above hydrolysis were fermented by yeast by the method of Saeman (18) and the

pentoses and pentosans estimated in terms of the unfermentable sugars.

3. Lignin: The difference between yield and total carbohydrates was expressed as noncarbohydrate material or lignin.

With each batch for analysis, a standard sample of uncooked aspen was also analyzed in order to reduce the errors introduced by incomplete saccharification of the pulps.

Preparation of Wood Samples

Air-dried aspen logs were cut to separate the sapwood from the heartwood. The sapwood pieces were reduced to sawdust in such a manner that the major portion was in the required screen size range. Other screen sizes from this batch were discarded. This procedure is necessary since, in order to compare rate data for various mesh sizes, the grinding must be such as to maintain the same ratio of lignin and carbohydrates in all the original samples. The different mesh sizes, each obtained from a different batch, were stored in glass bottles with tight-fitting covers. Moisture content was determined by the usual oven-drying method.

Variables Investigated

The range of variables investigated are given below.

1. Temperature:

   150°, 170°, 190° C. in the steam digester.

   200°, 210°, 220° C. in the salt bath.

2. Time:

   2 to 120 minutes for 150°, 170° and 190° C.

   1 to 20 minutes for 200°, 210°, and 220° C.

3. Liquor-wood ratio:

   10, 20, 40 and 80 at 170° C.

   The bulk of the experiments, where this ratio was not a variable, was carried out at 40 to 1 ratio.
4. Concentration of sodium sulfite:

   25, 50, 75 and 100 grams per liter of water at 170° C.

   12.5, 25, 50 and 100 grams per liter of water at 220° C.
5. Mesh size:

   Passing 5 and retained by 10.

   Passing 20 and retained by 40.

   Passing 60 and retained by 80.

   The bulk of the experiments, where mesh size was not a variable, was carried out at 20-40 mesh.

CHAPTER IV

DISCUSSION OF RESULTS

The experimental results and the corresponding graphs are shown in figures 4 to 10, which show the plots of total yield and of removal of total carbohydrates, pentosans and lignin, respectively, against time for all the temperatures investigated. Curves for total yield, and removal of pentosans and lignin at 200°, 210°, and 220° C. are shown on an enlarged scale in figures 8, 9, and 10, since at these temperatures the total period of cooking did not exceed 20 minutes. Yield is plotted as the percent total residue of the original oven-dried wood. Carbohydrates, pentosans and lignin are plotted as the percent removed of the amounts originally present.

Total Yield

The total yield decreases hyperbolically with time (figs. 4 and 8). A comparison of these curves with similar curves obtained by previous workers has been considered. In most of the previous work, the initial, high-reaction rate portions of the curves were either ignored or assumed to follow the same equation as the later and more accurate portions. In this investigation more emphasis is placed on the initial stages, since at high temperatures the higher yields are obtained only in these early stages.

The so-called energies of activation for different yields were calculated by assuming that the reaction followed a first-order rate equation with the rate constant expressed by the usual Arrhenius equation, thus

$$k = A\,e^{\frac{-E}{RT}}$$

where k = reaction velocity constant, 1/minute,

E = energy of activation, calories per gram mole,

A = frequency factor,

T = temperature in °K.

The instantaneous reaction rate was determined at each temperature from the slopes of the curves at a constant yield. Then from the first-order equation, k was determined, thus

$$r = -\frac{dx}{dt} = kx$$

where x = percent yield,

k = reaction velocity constant.

The logarithms of the velocity constants were plotted (fig. 11) against the reciprocals of the absolute temperatures at various parameters of constant yield. From the slopes of these lines the activation energies were calculated for the different yields. Table 3 gives the values of the reaction velocity "constants" for the different temperatures for various values of constant yields. The values of the activation energies, E, for the same yields are shown in table 4. From this table it is clear that the activation energy increases with increase in the loss of wood substance. This follows from the structural heterogeneity of the wood, the less-resistant portions hydrolyzing first and hence requiring less energy of activation.

Table 3.--Reaction Velocity "Constants" for Various Yields

Yield	Reaction velocity constant, k				
	Temperature (°C.)				
	220	210	200	190	170
Percent					
90	0.1162	0.0890	0.0560	0.0440	0.0261
85	.0705	.0548	.0356	.0274	.01105
80	.0562	.0415	.0275	.0201	.00722
75	.0462	.0317	.0164	....	....
70	.0386	.0246	.0058	....	....

Table 4.--Energies of Activation for Various Yields

Yield	Energy of activation
Percent	Calories per gram mole
90	13,850
85	14,000
80	15,500
75	22,700

Total Carbohydrates, Pentosans and Lignin

The removal of total carbohydrates and pentosans proceeds very fast at first. The corresponding curves (figs. 5 and 6) tend to flatten out with increased times of cooking. This tendency is greater with the pentosans than with the total carbohydrate material. Also, more of the pentosans are removed than the total carbohydrates, indicating the more easily hydrolyzable nature of the pentosans. Comparison of the data at 220° C. (figs. 5 and 6) shows that at the end of a 20-minute cook corresponding to a yield of 51.5 percent, the rates of removal are:

pentosans = 0.28 gram per 100 grams of original per minute.

carbohydrates = 0.48 gram per 100 grams of original per minute.

Thus, while the rate of pentosans removal at this yield is less than the rate of carbohydrates removal, the early rate of pentosan removal predominates so that at the end of 20 minutes more pentosans are removed than carbohydrates.

Another interesting observation is the fact that the latter, almost straight portions of these curves (figs. 5 and 6) do not extrapolate to the same point. Nickerson (14) has suggested that the "straight" portion of such a curve represents the "crystalline" constituents of the material being removed, while the initial part corresponds to the "amorphous" sections which due to their very nature are removed faster. With this interpretation, the straight portions should extrapolate to the same point. The failure of this common extrapolation can be better explained by supposing that temperature changes bring about a transformation of the crystalline to the amorphous forms.

By procedures similar to those used for total pulp yield, the velocity "constants" for pentosan removal were determined (table 5 and fig. 12). In these calculations, the amount of pentosans at any instant was expressed as percent of the original amount of pentosans present in the wood. The so-called energies of activation were also determined for various parameters of constant pentosan removal (table 6).

Table 5.--Reaction Velocity "Constants" for Various Degrees of Pentosan Removal

Pentosans removed (Percent of original)	Velocity constant, k			
	Temperature (°C.)			
	220	210	200	190
20	0.275	0.169	0.109	0.045
30	0.231	0.119	0.0677	0.00625
40	0.156	0.0562	0.0141	
50	0.160	0.0215	....	

Table 6.--Energies of Activation for Various Degrees of Pentosan Removal

Pentosans removed (Percent of original)	Energy of activation (Calories per gram mole)
20	24,700
30	31,500
40	51,800

It is seen from tables 5 and 6 that the removal of pentosans becomes more difficult as the reaction proceeds. A similar behavior is observed for the removal of lignin (table 7) and (fig. 13).

Table 7.--**Energies of Activation for Various Degrees of Delignification**

Lignin removed (Percent of original)	Energy of activation (Calories per gram mole)
20	4,600
30	5,600
40	5,800
50	9,100

The energy of activation for lignin removal is lower than the energy of activation for pentosan removal for temperatures between 190° C. and 220° C. Lignin should, therefore, be more easily removed than the pentosans if each is a separate reaction and independent of the other. The comparison of the rates of removal for specific parameters of constant yield will be considered in another section.

Liquor-wood Ratio

The effect of increasing this ratio is to decrease the yield, and increase the removal of pentosans and lignin. This increase in delignification and pentosan removal is insignificant in the yield range from 75 to 100 percent. At lower yields, however, the effect of this ratio is much more pronounced, particularly with pentosan removal (fig. 14).

Mesh-size of the Wood

The three mesh sizes investigated showed no decrease either in the rate of delignification or of pentosan removal with an increase in mesh size. There was, however, some slight but irregular variation in the total yields. This fact is attributable to errors in experiment. It can therefore be concluded that the resistance offered to diffusion of the liquid reactant is negligible on the rate of removal of wood constituents. Diffusion experiments on wood have shown that it takes only a few seconds for a 50-mesh sample to become uniformly saturated with the liquid. In the size range investigated, therefore, the time taken for the liquid to diffuse into the cell walls is negligible. This has been borne out in these experiments by the negligible effect of mesh size.

Rate Curves

Wherever convenient, the parameter "time" has been replaced by "yield," which is a more significant quantity in visualizing the pulping reactions. In table 8 are given the rates of pentosan and lignin removal for the various yields in the range 70 to 100 percent for the different temperatures investigated.

Table 6.--Rates of Pentosan and Lignin Removal

Temperature (°C.)	220	210	200	190	170
90 percent yield					
Rate of pentosan removal, grams per 100 grams per minute	25.0	17.25	11.0	5.20	2.8
Rate of lignin removal, grams per 100 grams per minute	20.00	15.25	9.00	4.40	1.2
85 percent yield					
Rate of pentosan removal, grams per 100 grams per minute	20.3	13.0	7.5	1.8	.24
Rate of lignin removal, grams per 100 grams per minute	16.5	12.8	7.5	3.4	.95
80 percent yield					
Rate of pentosan removal, grams per 100 grams per minute	15.0	8.83	3.9	.932	.08
Rate of lignin removal, grams per 100 grams per minute	13.25	9.67	5.5	1.45	.095

The rates of pentosan removal are plotted against reciprocal absolute temperatures for different yields in figure 15. It is seen from these curves that around 190° C., the rate curve for each of the yields shows a distinct break in its slope. Below 190° C., the rates of pentosan removal are very low, while above this temperature the rates increase tremendously. This behavior is not attributable to the change in the experimental cooking technique for temperatures at and above 200° C., since in that case the rise in the rate curves should have occurred at 200° C. instead of the indicated 190° C. It is possible to explain this increase in rate from the wood structure as representing a decrease in the over-all availability of the pentosans as cooking proceeds.

A sketch of the wood cell is shown in plate 4. Following the work of Kerr and Bailey (12), wood structure can be reduced to two main elements.

1. The network of intercellular material which completely surrounds each cell and is continuous throughout the structure.

2. The wood cell which is composed of the lumen in the center, then the secondary wall, followed by the cambial or the primary wall.

For all practical purposes the intercellular material consists of lignin and polyuronides; the secondary wall is composed of carbohydrates and lignin, the concentration of the lignin increasing toward the outer layer; and the cambial wall is composed of carbohydrates, lignin and polyuronides. It can be assumed that the pentosans behave similar to the total carbohydrate fraction, although they are removed relatively faster. A discussion of the carbohydrates of the wood structure can, therefore, be logically extended to apply to the pentosans.

At temperatures below 190° C., the carbohydrates from the outer layer, viz, the cambial wall, alone are removed. Had the reaction gone to completion at these temperatures, the carbohydrates from the primary wall would first be completely removed before the carbohydrates from the secondary wall enter the reaction. But as this temperature is reached the distinction between the carbohydrate fractions of the two walls becomes less marked so that all the carbohydrates are at once available for reaction, thus accounting for the change in the rate of their removal. Had this change not occurred, the rate would have increased along the curve extrapolated from lower temperatures (below 190° C.). It is, therefore, evident that the kinetics of carbohydrates removal are closely linked with the structure of the wood itself, and unless more is known about the quantitative distribution of the various wood components on the cell walls, no precise kinetic analysis is possible.

In the case of lignin removal, an identical behavior is noticed (table 8 and figure 16). The break in the curve occurs around 195° C. Bixler has reported (5) that soda and kraft liquors have a selective action on the ligneous portions of the wood. These liquors remove the intercellular lignin very rapidly but do not attack the cell-wall lignin to any extent until the former is completely removed. Sulfite liquors, on the other hand, do not show this selective action. The present postulation of a selective action of sodium sulfite liquor at lower temperatures is, therefore, not an entirely new concept. But the assumption that such selective action is destroyed at higher temperatures was not made in any previous investigations. While in pentosan removal the distinction was between the carbohydrates distributed in the two cell walls, here the distinction is between the main body of the lignin in the intercellular material and the lignin in the cell walls (both primary and secondary). At higher temperatures the entire lignin portion of the wood structure becomes simultaneously available, thus causing a changed rate of delignification.

Choice of Temperatures

In table 9 are given the rates of pentosan and lignin removal for various yields at the specific temperatures investigated. These rates are plotted graphically against yield for the different temperatures (figure 17). It is seen from this figure that at 220° C., above a yield of 76 percent, pentosan removal proceeds faster than lignin removal, while below this yield lignin removal is the faster. This reversal in the relative rates occurs at different yields for the different temperatures (table 10 and fig. 18). These "critical yields" decrease with increasing temperature. This information is useful in selecting the most desirable temperature for a required pulp quality (and quantity). Figure 18 represents the critical yields that can favorably be obtained (from aspen wood) for a given series of temperatures. Yields above this critical yield are considered undesirable. At a given temperature, cooking times should be extended to give yields slightly less than the critical yield.

Table 9.--Rates of Pentosan and Lignin Removal For Different Yields at Specific Temperatures

Temperature	Yield	Rate of pentosan removal	Rate of lignin removal
°C.	Percent	Gm. per 100 gm. per min.	Gm. per 100 gm. per min.
220	90	25.0	20.0
	85	20.3	16.5
	80	15.0	13.25
	75	9.5	10.8
	70	5.0	8.2
210	90	17.25	15.25
	85	13.0	12.8
	80	8.83	9.67
	75	3.8	6.1
	70	1.5	3.44
200	90	11.0	9.0
	85	7.5	7.5
	80	3.9	5.5
	75	1.4	3.3
	70	.43	.43

(continued)

Table 9.--Rates of Pentosan and Lignin Removal For Different Yields at Specific Temperatures (continued)

Temperature	Yield	Rate of pentosan removal	Rate of lignin removal
°C.	Percent	Gm. per 100 gm. per min.	Gm. per 100 gm. per min.
190	90	5.2	4.4
	85	1.8	3.4
	80	.932	1.45
	75	.445	....
	70	.283	.23

Table 10.--"Critical Yields" for Different Temperatures

Temperature	Critical yield
°C.	Percent
220	76.0
210	81.5
200	84.0
190	87.5

An inspection of table 10 shows that with increasing temperatures, the critical yield diminishes. At 220° C., yields above 76 percent are unfavorable, while at 190° C. the favorable range extends up to 87.5

percent. Similar data at lower temperatures were not obtained experimentally, but can be secured by extrapolation of the critical yield curve of figure 18.

The above facts need not, however, disfavor the use of high temperatures. If, for instance, a yield of 75 percent is required, instead of using 170° C., which is the usual industrial temperature, a temperature of 210° C. may be employed with a reduction in cooking time from about 2 hours to 5 minutes, and with little loss in pulp quality (from the standpoint of its pentosan and lignin contents). The final choice of temperature will be dictated by circumstances peculiar to any given operation. Curves such as these (fig. 18) might guide such choice in the initial stages.

The Effect of Concentration

In order to make the results more useful, runs were made at various concentrations at two different temperatures. The temperatures chosen were 170° C., the normal pulping temperature used in industry, and 220° C., the highest temperature used in the present experiments.

At 170° C. the concentration of sodium sulfite has little effect on the total pulp yield. The slight and irregular variations in the yield values as shown in series 2 of experimental results (see appendix) are statistically insignificant. The rates of removal of the pentosans and the lignin are, however, affected differently by changes in the liquor concentration. This fact is useful since it is possible to determine from these data the concentration most suitable for a desired pulp quality.

Figure 19 shows the percent of original pentosans removed for different times of cooking at concentrations of 25, 50, 75 and 100 grams sodium sulfite per liter of water. The influence of concentration for a given pulp yield was difficult to interpret from these curves. The data were, therefore, replotted in a more useful form. In table 11 are shown the amounts of pentosans removed for different concentrations at certain specific yields (in the high yield range). These data are graphically represented in figure 20. It is clearly seen from this figure that the effect of liquor concentration is quite marked in this yield range. There exists a particular concentration at which the pentosan removal is at a minimum. Rawlings and Staidl have stated (<u>15</u>) that the concentration has no effect on the rate of pentosan removal. This was probably because their work was limited in large measure to yields below 75 percent.

Table 11.--<u>Pentosans Removed for Different Concentrations at 170° C.</u>

Yield	Pentosans removed (percent of original)			
	Sodium sulfite concentration, grams per liter			
	25	50	75	100
<u>Percent</u>	<u>Percent</u>	<u>Percent</u>	<u>Percent</u>	<u>Percent</u>
90	23.0	14.8	12.6	26.4
85	28.7	18.0	20.2	31.5
80	38.0	35.0	32.5	36.7
75	47.5	40.5	41.0	40.5

A similar plotting of lignin values afforded no useful information (table 12). Therefore, in order to get the effect of concentration on lignin removal, curves of the type shown in figure 21 were prepared, where the ratio of pentosan removal to delignification is considered rather than straight pentosan or lignin values. The data for these plots are given in table 13.

Table 12.--Lignin Removed for Different Na_2SO_3 Concentrations at 170° C.

Yield	Lignin removed (percent of original)		
	Sodium sulfite concentration -- grams per liter		
Percent	25	50	75
90	7.3	11.9	9.8
85	14.2	19.3	20.2
80	33.3	36.1	32.5
75	45.9	45.6	44.6

Table 13.--Ratio of Pentosans to Lignin Removed at Different Na_2SO_3 Concentrations at 170° C.

Yield	Ratio of pentosans to lignin removed		
	Sodium sulfite concentration -- grams per liter		
	25	50	75
Percent			
90	2.5	1.24	1.285
85	2.02	.932	.960
80	1.15	.970	1.00
75	.882	.890	.908

It is evident from figure 21 that in the yield range considered, concentrations of less than 50 grams per liter are unfavorable. If one is interested only in the minimum removal of pentosans, a concentration of between 65 and 75 grams per liter is seen to be most desirable (fig. 20). On the other hand, if a maximum delignification is also desired, together with minimum pentosan removal (in the high yield range) a concentration of 50 grams per liter is favored, although higher concentrations will perform equally well.

The results at 220° C. were treated in an identical manner. The variation of yield with concentration is more pronounced in this case (fig. 22). The reversal in pentosan removal that was noticed at 170° C. (fig. 20) is not shown for the total yield at 220° C. Neither is such a reversal shown for the pentosan removal (fig. 23). This absence of reversal either in total yield or pentosan removal can be explained as follows.

Normally, the effect of concentration of the cooking liquor should be uniform either in decreasing the pentosan removal or increasing it. Since pure water removes the pentosans to a greater extent (1) than solutions of sodium sulfite, one would expect that with the increase in sodium sulfite concentration, the loss of pentosans will decrease. It is probable that with an increase in sodium sulfite concentration, two distinct reactions for pentosan removal come into play, viz, salt formation and hydrolysis. In the lower concentration range, as the salt concentration is increased, the excess salt suppresses hydrolysis, thus accounting for a decreased pentosan removal. In this region the rate of salt formation with the uronic acid groups associated with the carbohydrates is very slow, but as the concentration of sodium sulfite is further increased, the rate of salt formation is also increased so that the total pentosan loss once again begins to rise. It should be noted that both these reactions are probably going on in the entire concentration range. But below a certain concentration for a certain temperature, hydrolysis is controlling, while above that concentration salt formation becomes controlling. Since the temperature coefficients of these two reactions are presumably different, it is reasonable to suppose that at a certain temperature salt formation becomes controlling even before the effect of hydrolysis is reduced by increasing sodium sulfite concentration. This accounts for the absence of the minima in the curves of figure 23, the data for which are given in table 14.

Table 14.--Pentosans Removed for Different Na_2SO_3 Concentrations at 220° C.

Yield	Pentosans removed (percent original)		
	Sodium sulfite concentration (grams per liter)		
	12.5	25.0	100
Percent			
90	24.0	21.0	19.0
85	33.0	30.1	25.0
80	42.2	40.0	34.0
75	52.1	46.05	42.0
70	58.9	56.0	49.10

The apparent discrepancy in the constant yield curves for the two temperatures (figs. 20 and 23) is, as pointed out earlier, due to two different reactions that interchange control. The graphical appearance of this effect can be overcome by plotting the ratio of pentosans removed to concentration against yield for the different concentrations. Data for such plots for the two temperatures are given in tables 15 and 16. These are graphically represented in figures 24 and 25. In this method of plotting, the appearance of minima in the curves at 170° C. is avoided. Therefore, while this form is useful for extrapolation and interpolation purposes, it affords no direct information as to the most desirable concentration for a given yield. Considering the curves for 170° C., (fig. 24), from a determination of their slopes, the following equations result:

At a sodium sulfite concentration of 25 grams per liter,

$P = 1.925\ y$;

at a sodium sulfite concentration of 50 grams per liter,

$P = 1.600\ y$;

at a sodium sulfite concentration of 100 grams per liter,

$P = 1.900\ y$;

where P = pentosans removed based on the original content in percent;

and y = yield in percent.

From these equations the presence of an optimum concentration is evident, although this does not show in figure 24.

Table 15.--Ratio of Pentosans Removed to Concentration of Liquor for Different Concentrations in the Yield Range, 70-100%, 170° C.

Na_2SO_3 concentration	Pentosans removed --basis of original	Pentosans removed: concentration	Yield
Gm. per liter	Percent		Percent
25	22.7	0.91	1.10
	28.0	1.12	85
	38.0	1.52	80
	47.5	1.90	75
50	14.00	.28	90
	18.0	.36	85
	34.0	.68	80
	41.0	.82	75
100	26.0	.26	90
	32.0	.32	85
	37.0	.37	80
	41.0	.41	75

Table 16.--Ratio of Pentosans Removed to Concentrations of Liquor for Different Concentrations in the Yield Range 70 to 100 percent, 220° C.

Na_2SO_3 concentration	Pentosans removed -- based on original	Pentosans removed: concentration	Yield
Gm. per liter	Percent		Percent
12.5	24.0	1.92	90
	32.8	2.62	85
	42.0	3.36	80
	52.0	4.16	75
	59.0	4.72	70
25	20.7	.828	90
	30.0	1.20	85
	40.0	1.60	80
	48.0	1.92	75
	55.9	2.24	70
50	18.2	.36	90
	21.8	.44	85
	38.5	.77	80
	44.7	.89	75
	52.0	1.04	70
100	19.0	.190	90
	25.1	.251	85
	34.0	.340	80
	42.5	.425	75
	49.3	.493	70

Mechanism of Pulping

The complex nature of the pulping reactions can be analysed by considering them as consisting of two main simple reactions, namely,

1. Removal of carbohydrates
2. Removal of noncarbohydrate material (lignin).

The total rate of pulping can then be expressed as the sum of these two rates.

Lignin Removal

The instantaneous rate of removal of lignin may be considered as being dependent upon the instantaneous fraction of lignin present and its availability. The availability of the lignin depends upon the instantaneous pulp content and is hence dependent upon both the lignin and total carbohydrate present. This rate of delignification can be expressed by the equation

$$r_1 = k_1 \text{ (availability of lignin) (amount of lignin present).}$$

This can be expressed as

$$r_1 = k_1 \left[1 - \alpha_1(x_1 + x_2) \right] x_1 = - \frac{dx_1}{dt} \quad \text{---------------(1)}$$

where

r_1 = rate of lignin removal (grams of lignin per gram of wood per minute),

x_1 = grams of residual lignin per gram of wood,

x_2 = grams of residual carbohydrates per gram of wood,

k_1 = reaction velocity constant,

α_1 = a constant, depending upon nature of wood.

Since all the graphs are in terms of original amount of lignin present in the wood, equation (1) can be modified to be directly applicable. Let

c_1 = grams of initial lignin per gram of wood

f_1 = fraction of lignin removed

$$\frac{c_1 - x_1}{c_1} = f_1$$

$$x_1 = c_1(1 - f_1) \quad \text{--------------------------(2)}$$

From equations (1) and (2), equations (3) and (4) result.

$$r_1 = k_1\left[1 - \alpha_1 \ (c_1 + c_2) - (c_1f_1 + c_2f_2)\right]$$

$$c_1(1 - f_1) \quad \text{---------(3)}$$

or

$$r_1 = k_1\left[1 - \alpha_1(1 - c_1f_1 - c_2f_2) \ c_1(1 - f_1)\right]$$

$$= -\frac{dx_1}{dt} \quad \text{---------(4)}$$

α_1 and k_1 can be evaluated by determining r_1 for any two values of pulp yield at a given temperature. With this value of α_1, k_1 for other temperatures can be evaluated.

Sample Calculation

210° C.

At 90 percent yield, $f_1 = 0.11$, $f_2 = 0.05$, $c_1 = 0.285$, and $c_2 = 0.715$.

Then,

$$r = -\frac{dx}{dt} = -0.0435 = k_1\left[1 - \alpha_1(1 - 0.0308 - 0.0357)\right](0.254)$$

or

$$- 0.171 = k_1(1 - 0.9335\alpha_1).$$

At 75 percent yield

$$- 0.0174 = k_1 \left[1 - \alpha_1(1 - 0.128 - 0.1265)\right] 0.157$$

or

$$- 0.11060 = k_1(1 - 0.7455\,{}_1).$$

Hence,

$$k_1 = 0.129$$

$$\alpha_1 = 2.49.$$

Similar calculations were made for 200° C. and 220° C. in the yield range 70-100 percent. The results are given in table 17.

Carbohydrate Removal

The instantaneous rate of removal of carbohydrates may be considered as being dependent upon the instantaneous fraction of carbohydrates present and their availability. The availability of the carbohydrates, as in the case of lignin, depends upon the instantaneous pulp content and hence upon the lignin and total carbohydrates present. This rate of carbohydrate removal can be expressed by the equation

$$r_2 = k_2 \left[1 - \alpha_2 (x_1 + x_2)\right] x_2$$

where k_2 = reaction velocity constant,

α_2 = a constant depending upon nature of wood.

Calculations similar to those for lignin removal were made.

$$\alpha_2 = 1.54$$

Values of k_2 are shown in table 17.

Table 17.

Temperature (°C.)	k_1	k_2
200	0.084	0.110
210	0.129	0.168
220	0.107	0.215

Using the Arrhenius equation for the effect of temperature on reaction velocity constant (figs. 26 and 27), k_1 and k_2 are expressed as follows:

$$k_1 = (1.1)(10)^6 \; e^{\left(-\frac{15,300}{RT}\right)} \quad \text{-------------}(5)$$

$$k_2 = (2.42)\; 10^6 \; e^{\left(-\frac{15,800}{RT}\right)} \quad \text{-------------}(6)$$

Hence the final equations are:

<u>Lignin</u>

$$r_1 = -\frac{dx_1}{dt} = (1.1)(10^6)\; e^{\left(-\frac{15,300}{RT}\right)} \; 1 - 2.49\,(x_1 = x_2)\; x_1 \text{---}(7)$$

<u>Carbohydrates</u>

$$r_2 = -\frac{dx_2}{dt} = (2.42)(10^6)\; e^{\left(-\frac{15,800}{RT}\right)} \; 1 - 1.54\,(x_1 = x_2)\; x_2 \text{---}(8)$$

$$r = r_1 = r_2 \quad \text{--------------------------------}(9)$$

Values of r_1 and r_2 calculated from equations (7) and (8) were compared with experimental values. In table 18 are shown the values for 200° C. The agreement between the experimental and calculated values is seen to be (table 19) very close (figs. 28 and 29). Experimentally obtained pulping rates were compared with the rates obtained from equation (9). Here again the agreement is close (fig. 30). Percent deviations for different yields are also tabulated (table 19). The deviations are small enough to warrant recommendation of equations (7), (8), and (9) for the yield range 70-100 percent.

Table 18.--Comparison of Calculated and Experimental Rates at 200° C.

Yield	Rate of lignin removal		Rate of carbohydrate removal		Total pulping rate	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
Percent						
90	0.0248	0.0256	0.0286	0.0295	0.0534	0.0537
80	0.0138	0.0157	0.0146	0.0147	0.0284	0.0274
75	0.00965	0.00941	0.00772	0.0075	0.01737	0.0154
70	0.00177	0.00153	0.00246	0.00187	0.00423	0.00429

Table 19.--Percent Deviation if Calculated From Experimental Rates

Yield	Percent deviation		
	Lignin removal	Pentosan removal	Pulp yield
Percent			
90	-3.2	-3.05	-0.57
80	-12.0	-0.67	+3.65
75	+2.55	+2.85	+13.0
70	+16.1	....	-1.4

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APPENDIX

L.K. Doraiswamy

THE KINETICS OF PULPING ASPEN WOOD
WITH SODIUM SULFITE SOLUTIONS

By

KRISHNAMURTHY DORAISWAMY

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requirements for the degree of
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SUMMARY

The object of this investigation was to determine the most favorable conditions of pulping aspen wood with solutions of sodium sulfite to obtain yields above 70 percent. The rates of removal of pentosans (the easily-removed fraction of the carbohydrate content of wood) and lignin were measured in order to determine the conditions favoring a minimum pentosan loss and a maximum lignin removal.

It was found that a critical yield exists for each temperature. The critical yield is defined as the yield at which the rate of lignin removal just equals the rate of pentosan removal. For a given temperature, therefore, it is advantageous to use cooking times which would result in pulp yields slightly less than the critical yield.

The effect of sodium sulfite concentration was examined. For the removal of pentosans, the liquor concentration shows an optimum value of 65 to 75 grams per liter at which there is a minimum loss of pentosans. For the combined requirement of a minimum pentosan loss and a maximum lignin removal, concentrations of less than 50 grams sodium sulfite per liter are unfavorable.

It was also found that the rate curves for lignin and pentosan removal (logarithmic rates plotted against reciprocal absolute temperatures) showed a sharp rise at high temperatures, indicating the possibility that the over-all availability of these wood fractions undergoes a change at high temperatures. This is attributed to structural changes in wood.

The mechanism of the complex pulping reactions may be explained by considering the over-all pulping reaction to be composed essentially of two general reactions, namely,

1. Removal of lignin
2. Removal of carbohydrates

Rates of each of these reactions can be expressed in terms of the instantaneous amount of that particular fraction and its availability. The availability of each fraction is dependent on the instantaneous total pulp content. On this basis, two independent rate equations have been derived for the removal of lignin and carbohydrates. The sum of these separate rates is the total rate of pulping. The mechanical correlation of data has been restricted tentatively to temperatures of 200°, 210°, and 220° C., and for yields above 70 percent. The agreement between the calculated and experimental rates and amounts of lignin, carbohydrate and total wood substance (yield) removal has been found to be within ± 5 percent.

The rate equations obtained are given below:

<u>For lignin removal</u>

$$r_1 = (1.1)\,(10^6)\,(e^{-\frac{15,300}{RT}})\left[1 - \alpha_1(x_1 + x_2)\right]x_1$$

<u>For carbohydrate removal</u>

$$r_2 = (2.42)\,(10^6)\,(e^{-\frac{15,800}{RT}})\left[1 - \alpha_2(x_1 + x_2)\right]x_2$$

<u>Total yield</u>

$$r = r_1 + r_2$$

where

r_1 = rate of lignin removal (grams per gram of wood per minute)

r_2 = rate of carbohydrate removal (grams per gram of wood per minute).

x_1 and x_2 are the instantaneous amounts of lignin and carbohydrates present, respectively.

α_1 and α_2 are constants depending on the nature of the wood.

For aspen wood,

$\alpha_1 = 2.49$

$\alpha_2 = 1.54$

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CHAPTER I

REASONS FOR INVESTIGATION

The object of this investigation was to increase knowledge concerning the mechanism of pulping wood with sodium sulfite solutions in producing a product of pulp in yields above 70 percent. There presently exists little fundamental information on the high-yield sodium sulfite pulping process which has recently become established as one of the major pulping methods of the wood pulp industry. The importance of this process in the potential conservation of forest resources and the utilization of all available species of woods, particularly the hardwoods, has also become well recognized. With the introduction of semichemical pulping, the use of sodium sulfite liquors has been greatly increased.

The study of the mechanism of the pulping of wood by any process is complicated because the actual constitutions of the two major fractions of the wood that influence the quality and the quantity of the pulps derived therefrom are to a great extent unknown; these fractions are the hemicelluloses associated with cellulose for the most part in the cell walls of the wood fibers, and the intercellular material which is predominantly lignin. Many formulae have been postulated for the lignin molecule, but there are strong reasons to believe that the lignin, as it occurs in wood, differs in constitution from the isolated lignin. In addition to the heterogeneity of the wood itself, each of the reactions involved in pulping is heterogeneous. This makes the study of the pulping reaction kinetics extremely complicated. The commonly used pulping agents heretofore have been calcium bisulfite in sulfurous acid for sulfite pulping, sodium hydroxide for soda pulping, and a mixture of sodium hydroxide and sodium sulfide for sulfate pulping. Of these, the sulfite process has received the most attention in kinetic studies. Most theories have been restricted to the delignification reaction with little speculation on the theories of hemicellulose removal. It is known, nevertheless, that during the early part of sulfite pulping the rate of removal of certain carbohydrates, mostly hemicelluloses, exceeds the rate of lignin removal because of the more easily hydrolyzable nature of these carbohydrates. It is also known that the rate of loss of carbohydrates is decreased relative to the rate of lignin removal in the later stages of the pulping reaction. It is apparent, therefore, that it is difficult to retain the much desired carbohydrates and at the same time to remove the unwanted lignin. In this respect, the results from the soda and the sulfate processes follow the same trend. On the other hand, it is possible to control to some extent the relative amounts of lignin and hemicelluloses removed, and their relative rates of removal, by using pulping reagents and procedures other than those commonly employed in the past.

CHAPTER II

PREVIOUS INVESTIGATIONS AND LITERATURE REVIEW

Cross in 1880 (9) was the first to suggest the use of sodium monosulfite for pulping wood. He proposed that the so-called lignocellulose was hydrolyzed by the sodium sulfite and that the reactive aldehydic and acidic groups of the lignin molecule were fixed by the sulfite and the basic groups, respectively, of the pulping liquor. Since the work of Cross the field remained almost unexplored until about 1920, when a significant commercial application was proposed by Bradley and McKeefe (6) for using sodium sulfite. Brot and Hirschell (8) determined the effect of sodium sulfite concentration on the over-all yield of pulp. In cooking cereal straw, they found that the yield of pulp at first decreased with increasing sodium sulfite concentration, reaching a minimum at a concentration of 4 percent. Above 4 percent the yield increased progressively. It was proposed that the rise in yield with concentrations above 4 percent was due to the inhibition of the erosive action of the liquor on the fiber, the excess sodium sulfite suppressing hydrolysis. Later studies by Rawlings and Staidl (15) were of a more comprehensive nature. They reported that the concentration of the sulfite had little effect, if any, on the removal of the various constituents of wood. Their data indicated that the complete removal of lignin would require temperatures at which the total yield of pulp would be less than 50 percent. Little nonlignin material was removed below 170° C., and it was suggested that 140° C. would be the best temperature for obtaining high yields, since at that temperature, though delignification would be incomplete, little cellulose would be destroyed.

From the data of Brunn on alkaline pulping, Arrhenius (4) suggested that the pulping of wood follows a first order rate equation. His "rate constant" was not constant over the range of conditions investigated.

Bray and Eastwood (6) have reported some interesting conclusions about delignification. Their experiments covered yields ranging from 85 to 60 percent, and temperatures of 140°, 150°, 160°, and 170° C. Using a 25-gram sample of wood and a sodium sulfite concentration of 50 grams per liter, they digested for periods ranging from 1 to 8 hours. Assuming the yield to decrease according to a modified first order equation, from the observation that the first order "rate constant" decreased with decreasing yield according to a certain pattern, they developed empirical equations for predicting the yield for a given time and temperature. For the delignification reaction, these workers assumed that one of the reactants, in this case the pulping chemical, remains constant as the reaction proceeds. This may be justified by the fact that the reagent molecules, being of small size, far outnumber the lignin molecules which are originally in a high state of polymerization. On this basis and on experimental evidence, a second order equation was proposed for delignification and another empirical equation derived.

Aronovsky and Gortner (3) studied the effect of sodium sulfite concentrations and temperatures on the rates of destruction of cellulose, pentosans, lignin and total wood substance. Using aspen sawdust and temperatures of 170° and 185° C., they made the following observations:

a. The original lignin was progressively destroyed as the salt-wood ratio was increased from zero to 0.238. Doubling this ratio resulted in a

slight but definite increase in lignin removal. Lignin removal, according to them, proceeds in two stages, namely by depolymerization followed by reaction between sodium sulfite and the products of depolymerization.
b. Pentosan removal was much less drastic than with either pure water, sodium sulfate, or sodium thiosulfate. Doubling the sulfite concentration, however, increased the rate of pentosan destruction, contrary to the effect in the low concentration range.
c. The destruction of cellulose was remarkably low, a situation most desirable for high-yield pulping.

Choice of Liquor

The use of water alone as a pulping reagent has limited application in semichemical pulping for high yields because the organic acids formed with the acid-forming groups in the wood remove little of the generally unwanted lignin and tend to destroy the pentosans and other carbohydrates instead (1). Since the hydrolysis of cellulose occurs by cooking wood in the presence of free acids and alkalies, the cooking should be done in a neutral medium to minimize the loss of cellulose. It is known that organic acids are released from wood during cooking so that a salt that would preserve a neutral or near-neutral state should be added. Sodium sulfite, being a salt of a weakly dissociated polybasic acid, exerts such a buffering action when used in excess. Of the many possible salts belonging to this category, sodium sulfite has been most used because of its relation to the soda process through the sodium ion on the one hand, and to the sulfite process through the sulfite ion on the other. Aronovsky and Gortner (2) have studied the effect of adding various salts on the rates of removal of lignin and pentosans. Their specific data on sodium sulfite pulping indicate the advantages of using this chemical (3). A further advantage is the fact that the semichemical process removes sufficient lignin to soften the chips and thus permits defibration by mechanical means into pulp composed substantially of individual fibers with paper-making qualities.

CHAPTER III

EXPERIMENTAL METHODS

The experimental technique employed in this investigation was divided into two parts. The work up to 190° C. was carried out in glass tubes placed in a pressure autoclave, referred to here as the steam digester. Above 190° C., a salt bath was used and stainless steel reactors were substituted for the glass tubes.

The Pressure Autoclave

A photograph of the pressure autoclave is shown in plate 1. This is the same autoclave as employed by Saeman in his wood hydrolysis experiments (16). The sealed glass tubes were tied to a copper rack that fits into the digester. The rack, together with the lid of the digester, was operated by a pulley and chain. The use of test tubes for small-size samples is advantageous in that many samples with different liquor concentrations and wood-liquor ratios can be easily cooked simultaneously under identical conditions for a given time and temperature. The collection of many simultaneous samples makes the data at different temperatures and different times of digestion much more comparable. In conducting a digestion, air was first driven out of the autoclave by operating the flush valves after which these valves were closed and the steam introduced until a pressure was built up in the digester corresponding to the required temperature, as indicated by the pressure gage. The valve which regulates the steam inlet maintains the temperature inside the digester constant to within 0.5° C.

The actual period of digestion was taken as that between the instant the pressure gage registered the desired pressure and the instant the steam blow-off was started. This requires consideration of the effect of the initial heating period in reaching the desired temperature of operation, and also the time required to reduce the steam pressure to atmospheric at the end of the run. A typical case may be considered, say 170° C. It is known that the pulping reaction rate is approximately doubled for each 10° C. rise in temperature. The normal heating and the blow-off periods are of the order of 1 minute each. The average temperature during the heating up to 170° C. is 140° C. The equivalent time at 170° C., therefore, would be one-fourth minute. Since this one-fourth minute appears in each run of the digester, its only effect, if neglected, would be to displace the time-yield curves along the time axis uniformly for all the runs at that temperature. The average temperature during the heating period for the other final temperatures investigated, namely 150° C. and 190° C., were 130° and 155° C., respectively. It is apparent that the equivalent time for the heating period for each of the temperatures is one-fourth minute or less. The rate of steam blow-off is so adjusted that the equivalent time for the blow-off period for each of the temperatures is also one-fourth minute. Thus for each run a total of one-half minute must be added to the "cooking time" as defined earlier.

The Molten Salt Bath

For temperatures of 200° C. and above, a molten mixture of the nitrates of sodium, potassium and lithium was used in the constant temperature bath. This bath was contained in an asbestos-covered container (plate 2) heated electrically by eight resistances in series. Large temperature adjustments were made by switching off one or more of the resistances as required. The salt bath was kept well stirred during the entire period of cooking. The final temperature was maintained constant by a thermal regulator to ± 0.1° C. Data on the properties of this salt mixture are available in the International Critical Tables (11). One of the advantages in using a salt bath is the fact that any salt adhering to the reactors can be easily removed by cooling and washing in cold water.

Reactors

The pulping reactions proceed very fast in the initial stages of cooking. In a batch reaction of this type, a small rise in temperature may result in a lowering of the reaction time from several hours to a few seconds. To secure temperature control, therefore, the reactors used for such rapid reactions must have:

a. high heat conductivity
b. adequate strength
c. low heat capacity
d. corrosion resistance

Details concerning such reactors with various metals of construction have been studied by Saeman and others (17). The reactors used in this present investigation were designed on the same lines (plate 3). Data on the reactors are given below.

Material: all parts coming in contact with the liquor of stainless steel; the rest of monel.

Length: 10 inches.

Diameter: 3/8 inch.

Volume: 4.43 cubic inches.

Stainless steel was chosen because (17) of its ability to withstand high internal pressures almost independent of temperature.

The reactors were suspended in the bath by the long-handle holder shown in plate 2.

Equivalent Time Calculations

From a knowledge of the temperature coefficient of the pulping reactions, it is known that at 200° C. or above, less than 20 minutes would be required for a yield of 70 percent. At these high temperatures for such short periods of cooking, the heating and the cooling periods have a significant effect and must, therefore, be properly accounted for.

The rate of heating of the reactors was estimated by measuring the time required for a thermocouple to reach various temperatures. This was done by welding the end of a copper-constantan thermocouple into the end of a 1/8-inch copper tubing. This end was placed in the reactor. The measured rate of temperature rise is less than the true rise due to the lag introduced by the thermocouple well and the measuring instrument.

Figure 1 shows the experimental curve obtained for a bath temperature of 200° C. Since the curves for the higher temperatures almost coincided with this curve, they are not shown separately. ΔT denotes the temperature difference between the bath and the reactor at any given instant of time. It is seen that 57 seconds are required for the reactor to reach 199.5° C. (for a bath temperature of 200° C.). In table 1 are given the values of the first order reaction rate constants for a few selected values of the reactor temperature. The rate constants at 150°, 170°, 190°, 200°, 210° and 220° C. were obtained experimentally by assuming the over-all pulping reaction to be unimolecular. For the intermediate values of the temperature (e.g., 195° C.), the velocity constants were calculated from the Arrhenius equation using an activation energy of 27,000 calories per gram mole, since this value represents the average value for the pulping reactions in the high yield range. A sample calculation of the equivalent time at 200° C. is shown below.

Table 1.--Time-temperature Relation for the Heating Period and the Corresponding Reaction Velocity Constants

Temperature inside reactor (T)	ΔT for a bath temperature of 200° C.	Time (t)	Velocity constant (k)
°C.	°C.	Seconds	(Min.) 10^3
150	50	19	0.2637
170	30	23	0.785
190	10	34	2.88
195	5	38	4.3
199.5	0.5	57	5.56

Plots of the velocity constants against time are shown for final temperatures of 200° C., 210° C., and 220° C. (fig. 2).

The area kt of the curve for $t = 57$ is 0.0023.

Assuming that the rate is given by the first order equation

$$-\frac{dx}{dt} = kx \quad \text{---------------} \quad (1)$$

where x = percent of original remaining in the wood we get, on integration

$$-\log x = \frac{kt}{2.303} \quad \text{-----------} \quad (2)$$

$$\log x = -\frac{0.0023}{2.303}$$

$$x = 99.8\%$$

Hence, amount converted = 0.2%.

Now, at 200° C., $k = 0.00581$.

Therefore, from equation (2),

$x = 90.75\%$ for 1000 seconds (arbitrarily taken).

The amount converted if the reaction were to proceed uniformly at 200° C. without a heating period would be 9.25 percent. Hence, equivalent time (defined as the time equivalent at the final temperature corresponding to the total reaction during the heating period)

$$= \frac{0.2}{9.25}(1000)$$

$$= 22 \text{ seconds.}$$

Similar calculations were made for 210° C. and 220° C. and the results are tabulated in table 2.

Table 2.--Equivalent Times for the Heating Period

Temperature	Equivalent time
°C.	Seconds
200	22
210	25
220	27

These values are shown graphically in figure 3.

Analytical Procedure

The size of the wood samples taken for analysis was 0.6 gram where the steam digester was used and 0.3 gram when the salt bath was employed. This reduction in sample size was necessary because a smaller reactor was used in the salt bath. The glass tubes were sealed after introducing the wood meal and liquor and cooked in the steam digester. After digestion the tubes were broken by an electric cutter and the contents washed into weighed Gooch crucibles with carbon dioxide-free distilled water. The residual pulps were dried overnight at 105° C. and analyzed as follows.

1. Carbohydrate material: This was analyzed in terms of potential reducing sugar after hydrolysis of the pulp with 72 percent sulfuric acid according to the technique developed by Saeman (18). The analysis of the sugars followed the method of Shaffer and Somogyi (19).

2. Pentoses and pentosans: The sugars obtained by the above hydrolysis were fermented by yeast by the method of Saeman (18) and the

pentoses and pentosans estimated in terms of the unfermentable sugars.

3. Lignin: The difference between yield and total carbohydrates was expressed as noncarbohydrate material or lignin.

With each batch for analysis, a standard sample of uncooked aspen was also analyzed in order to reduce the errors introduced by incomplete saccharification of the pulps.

Preparation of Wood Samples

Air-dried aspen logs were cut to separate the sapwood from the heartwood. The sapwood pieces were reduced to sawdust in such a manner that the major portion was in the required screen size range. Other screen sizes from this batch were discarded. This procedure is necessary since, in order to compare rate data for various mesh sizes, the grinding must be such as to maintain the same ratio of lignin and carbohydrates in all the original samples. The different mesh sizes, each obtained from a different batch, were stored in glass bottles with tight-fitting covers. Moisture content was determined by the usual oven-drying method.

Variables Investigated

The range of variables investigated are given below.

1. Temperature:

   150°, 170°, 190° C. in the steam digester.

   200°, 210°, 220° C. in the salt bath.

2. Time:

   2 to 120 minutes for 150°, 170° and 190° C.

   1 to 20 minutes for 200°, 210°, and 220° C.

3. **Liquor-wood ratio:**

   10, 20, 40 and 80 at 170° C.

   The bulk of the experiments, where this ratio was not a variable, was carried out at 40 to 1 ratio.

4. **Concentration of sodium sulfite:**

   25, 50, 75 and 100 grams per liter of water at 170° C.

   12.5, 25, 50 and 100 grams per liter of water at 220° C.

5. **Mesh size:**

   Passing 5 and retained by 10.

   Passing 20 and retained by 40.

   Passing 60 and retained by 80.

   The bulk of the experiments, where mesh size was not a variable, was carried out at 20-40 mesh.

CHAPTER IV

DISCUSSION OF RESULTS

The experimental results and the corresponding graphs are shown in figures 4 to 10, which show the plots of total yield and of removal of total carbohydrates, pentosans and lignin, respectively, against time for all the temperatures investigated. Curves for total yield, and removal of pentosans and lignin at 200°, 210°, and 220° C. are shown on an enlarged scale in figures 8, 9, and 10, since at these temperatures the total period of cooking did not exceed 20 minutes. Yield is plotted as the percent total residue of the original oven-dried wood. Carbohydrates, pentosans and lignin are plotted as the percent removed of the amounts originally present.

Total Yield

The total yield decreases hyperbolically with time (figs. 4 and 8). A comparison of these curves with similar curves obtained by previous workers has been considered. In most of the previous work, the initial, high-reaction rate portions of the curves were either ignored or assumed to follow the same equation as the later and more accurate portions. In this investigation more emphasis is placed on the initial stages, since at high temperatures the higher yields are obtained only in these early stages.

The so-called energies of activation for different yields were calculated by assuming that the reaction followed a first-order rate equation with the rate constant expressed by the usual Arrhenius equation, thus

$$k = A\,e^{\frac{-E}{RT}}$$

where k = reaction velocity constant, 1/minute,

E = energy of activation, calories per gram mole,

A = frequency factor,

T = temperature in °K.

The instantaneous reaction rate was determined at each temperature from the slopes of the curves at a constant yield. Then from the first-order equation, k was determined, thus

$$r = -\frac{dx}{dt} = kx$$

where x = percent yield,

k = reaction velocity constant.

The logarithms of the velocity constants were plotted (fig. 11) against the reciprocals of the absolute temperatures at various parameters of constant yield. From the slopes of these lines the activation energies were calculated for the different yields. Table 3 gives the values of the reaction velocity "constants" for the different temperatures for various values of constant yields. The values of the activation energies, E, for the same yields are shown in table 4. From this table it is clear that the activation energy increases with increase in the loss of wood substance. This follows from the structural heterogeneity of the wood, the less-resistant portions hydrolyzing first and hence requiring less energy of activation.

Table 3.--Reaction Velocity "Constants" for Various Yields

Yield	Reaction velocity constant, k				
	Temperature (°C.)				
	220	210	200	190	170
Percent					
90	0.1162	0.0890	0.0560	0.0440	0.0261
85	.0705	.0548	.0386	.0274	.01105
80	.0562	.0415	.0275	.0201	.00722
75	.0462	.0317	.0164	....	....
70	.0386	.0246	.0058	....	....

Table 4.--Energies of Activation for Various Yields

Yield	Energy of activation
Percent	Calories per gram mole
90	13,850
85	14,000
80	15,500
75	22,700

Total Carbohydrates, Pentosans and Lignin

The removal of total carbohydrates and pentosans proceeds very fast at first. The corresponding curves (figs. 5 and 6) tend to flatten out with increased times of cooking. This tendency is greater with the pentosans than with the total carbohydrate material. Also, more of the pentosans are removed than the total carbohydrates, indicating the more easily hydrolyzable nature of the pentosans. Comparison of the data at 220° C. (figs. 5 and 6) shows that at the end of a 20-minute cook corresponding to a yield of 51.5 percent, the rates of removal are:

pentosans = 0.28 gram per 100 grams of original per minute.

carbohydrates = 0.48 gram per 100 grams of original per minute.

Thus, while the rate of pentosans removal at this yield is less than the rate of carbohydrates removal, the early rate of pentosan removal predominates so that at the end of 20 minutes more pentosans are removed than carbohydrates.

Another interesting observation is the fact that the latter, almost straight portions of these curves (figs. 5 and 6) do not extrapolate to the same point. Nickerson (14) has suggested that the "straight" portion of such a curve represents the "crystalline" constituents of the material being removed, while the initial part corresponds to the "amorphous" sections which due to their very nature are removed faster. With this interpretation, the straight portions should extrapolate to the same point. The failure of this common extrapolation can be better explained by supposing that temperature changes bring about a transformation of the crystalline to the amorphous forms.

By procedures similar to those used for total pulp yield, the velocity "constants" for pentosan removal were determined (table 5 and fig. 12). In these calculations, the amount of pentosans at any instant was expressed as percent of the original amount of pentosans present in the wood. The so-called energies of activation were also determined for various parameters of constant pentosan removal (table 6).

Table 5.--Reaction Velocity "Constants" for Various Degrees of Pentosan Removal

Pentosans removed (Percent of original)	Velocity constant, k			
	Temperature (°C.)			
	220	210	200	190
20	0.275	0.169	0.109	0.045
30	0.231	0.119	0.0577	0.00625
40	0.156	0.0562	0.0141	
50	0.160	0.0215	....	

Table 6.--Energies of Activation for Various Degrees of Pentosan Removal

Pentosans removed (Percent of original)	Energy of activation (Calories per gram mole)
20	24,700
30	31,500
40	51,800

It is seen from tables 5 and 6 that the removal of pentosans becomes more difficult as the reaction proceeds. A similar behavior is observed for the removal of lignin (table 7) and (fig. 13).

Table 7.--Energies of Activation for Various Degrees of Delignification

Lignin removed (Percent of original)	Energy of activation (Calories per gram mole)
20	4,600
30	5,600
40	5,800
50	9,100

The energy of activation for lignin removal is lower than the energy of activation for pentosan removal for temperatures between 190° C. and 220° C. Lignin should, therefore, be more easily removed than the pentosans if each is a separate reaction and independent of the other. The comparison of the rates of removal for specific parameters of constant yield will be considered in another section.

Liquor-wood Ratio

The effect of increasing this ratio is to decrease the yield, and increase the removal of pentosans and lignin. This increase in delignification and pentosan removal is insignificant in the yield range from 75 to 100 percent. At lower yields, however, the effect of this ratio is much more pronounced, particularly with pentosan removal (fig. 14).

Mesh-size of the Wood

The three mesh sizes investigated showed no decrease either in the rate of delignification or of pentosan removal with an increase in mesh size. There was, however, some slight but irregular variation in the total yields. This fact is attributable to errors in experiment. It can therefore be concluded that the resistance offered to diffusion of the liquid reactant is negligible on the rate of removal of wood constituents. Diffusion experiments on wood have shown that it takes only a few seconds for a 50-mesh sample to become uniformly saturated with the liquid. In the size range investigated, therefore, the time taken for the liquid to diffuse into the cell walls is negligible. This has been borne out in these experiments by the negligible effect of mesh size.

Rate Curves

Wherever convenient, the parameter "time" has been replaced by "yield," which is a more significant quantity in visualizing the pulping reactions. In table 8 are given the rates of pentosan and lignin removal for the various yields in the range 70 to 100 percent for the different temperatures investigated.

Table 8.--Rates of Pentosan and Lignin Removal

Temperature (°C.)	220	210	200	190	170
90 percent yield					
Rate of pentosan removal, grams per 100 grams per minute	25.0	17.25	11.0	5.20	2.8
Rate of lignin removal, grams per 100 grams per minute	20.00	15.25	9.00	4.40	1.2
85 percent yield					
Rate of pentosan removal, grams per 100 grams per minute	20.3	13.0	7.5	1.8	.24
Rate of lignin removal, grams per 100 grams per minute	16.5	12.8	7.5	3.4	.95
80 percent yield					
Rate of pentosan removal, grams per 100 grams per minute	15.0	8.83	3.9	.932	.08
Rate of lignin removal, grams per 100 grams per minute	13.25	9.67	5.5	1.45	.095

The rates of pentosan removal are plotted against reciprocal absolute temperatures for different yields in figure 15. It is seen from these curves that around 190° C., the rate curve for each of the yields shows a distinct break in its slope. Below 190° C., the rates of pentosan removal are very low, while above this temperature the rates increase tremendously. This behavior is not attributable to the change

in the experimental cooking technique for temperatures at and above 200° C., since in that case the rise in the rate curves should have occurred at 200° C. instead of the indicated 190° C. It is possible to explain this increase in rate from the wood structure as representing a decrease in the over-all availability of the pentosans as cooking proceeds.

A sketch of the wood cell is shown in plate 4. Following the work of Kerr and Bailey (12), wood structure can be reduced to two main elements.

1. The network of intercellular material which completely surrounds each cell and is continuous throughout the structure.

2. The wood cell which is composed of the lumen in the center, then the secondary wall, followed by the cambial or the primary wall.

For all practical purposes the intercellular material consists of lignin and polyuronides; the secondary wall is composed of carbohydrates and lignin, the concentration of the lignin increasing toward the outer layer; and the cambial wall is composed of carbohydrates, lignin and polyuronides. It can be assumed that the pentosans behave similar to the total carbohydrate fraction, although they are removed relatively faster. A discussion of the carbohydrates of the wood structure can, therefore, be logically extended to apply to the pentosans.

At temperatures below 190° C., the carbohydrates from the outer layer, viz, the cambial wall, alone are removed. Had the reaction gone to completion at these temperatures, the carbohydrates from the primary wall would first be completely removed before the carbohydrates from the secondary wall enter the reaction. But as this temperature is reached the distinction between the carbohydrate fractions of the two walls becomes less marked so that all the carbohydrates are at once available for reaction, thus accounting for the change in the rate of their removal. Had this change not occurred, the rate would have increased along the curve extrapolated from lower temperatures (below 190° C.). It is, therefore, evident that the kinetics of carbohydrates removal are closely linked with the structure of the wood itself, and unless more is known about the quantitative distribution of the various wood components on the cell walls, no precise kinetic analysis is possible.

In the case of lignin removal, an identical behavior is noticed (table 8 and figure 16). The break in the curve occurs around 195° C. Bixler has reported (5) that soda and kraft liquors have a selective action on the ligneous portions of the wood. These liquors remove the intercellular lignin very rapidly but do not attack the cell-wall lignin to any extent until the former is completely removed. Sulfite liquors, on the other hand, do not show this selective action. The present postulation of a selective action of sodium sulfite liquor at lower temperatures is, therefore, not an entirely new concept. But the assumption that such selective action is destroyed at higher temperatures was not made in any previous investigations. While in pentosan removal the distinction was between the carbohydrates distributed in the two cell walls, here the distinction is between the main body of the lignin in the intercellular material and the lignin in the cell walls (both primary and secondary). At higher temperatures the entire lignin portion of the wood structure becomes simultaneously available, thus causing a changed rate of delignification.

Choice of Temperatures

In table 9 are given the rates of pentosan and lignin removal for various yields at the specific temperatures investigated. These rates are plotted graphically against yield for the different temperatures (figure 17). It is seen from this figure that at 220° C., above a yield of 76 percent, pentosan removal proceeds faster than lignin removal, while below this yield lignin removal is the faster. This reversal in the relative rates occurs at different yields for the different temperatures (table 10 and fig. 18). These "critical yields" decrease with increasing temperature. This information is useful in selecting the most desirable temperature for a required pulp quality (and quantity). Figure 18 represents the critical yields that can favorably be obtained (from aspen wood) for a given series of temperatures. Yields above this critical yield are considered undesirable. At a given temperature, cooking times should be extended to give yields slightly less than the critical yield.

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Table 9.--Rates of Pentosan and Lignin Removal For Different Yields at Specific Temperatures

Temperature	Yield	Rate of pentosan removal	Rate of lignin removal
°C.	Percent	Gm. per 100 gm. per min.	Gm. per 100 gm. per min.
220	90	25.0	20.0
	85	20.3	16.5
	80	15.0	13.25
	75	9.5	10.8
	70	5.0	8.2
210	90	17.25	15.25
	85	13.0	12.8
	80	8.83	9.67
	75	3.8	6.1
	70	1.5	3.44
200	90	11.0	9.0
	85	7.5	7.5
	80	3.9	5.5
	75	1.4	3.3
	70	.43	.43

(continued)

Table 9.--Rates of Pentosan and Lignin Removal For Different Yields at Specific Temperatures (continued)

Temperature	Yield	Rate of pentosan removal	Rate of lignin removal
°C.	Percent	Gm. per 100 gm. per min.	Gm. per 100 gm. per min.
	90	5.2	4.4
	85	1.8	3.4
190	80	.932	1.45
	75	.445	....
	70	.283	.23

Table 10.--"Critical Yields" for Different Temperatures

Temperature	Critical yield
°C.	Percent
220	76.0
210	81.5
200	84.0
190	87.5

An inspection of table 10 shows that with increasing temperatures, the critical yield diminishes. At 220° C., yields above 76 percent are unfavorable, while at 190° C. the favorable range extends up to 87.5

percent. Similar data at lower temperatures were not obtained experimentally, but can be secured by extrapolation of the critical yield curve of figure 18.

The above facts need not, however, disfavor the use of high temperatures. If, for instance, a yield of 75 percent is required, instead of using 170° C., which is the usual industrial temperature, a temperature of 210° C. may be employed with a reduction in cooking time from about 2 hours to 5 minutes, and with little loss in pulp quality (from the standpoint of its pentosan and lignin contents). The final choice of temperature will be dictated by circumstances peculiar to any given operation. Curves such as these (fig. 18) might guide such choice in the initial stages.

The Effect of Concentration

In order to make the results more useful, runs were made at various concentrations at two different temperatures. The temperatures chosen were 170° C., the normal pulping temperature used in industry, and 220° C., the highest temperature used in the present experiments.

At 170° C. the concentration of sodium sulfite has little effect on the total pulp yield. The slight and irregular variations in the yield values as shown in series 2 of experimental results (see appendix) are statistically insignificant. The rates of removal of the pentosans and the lignin are, however, affected differently by changes in the liquor concentration. This fact is useful since it is possible to determine from these data the concentration most suitable for a desired pulp quality.

Figure 19 shows the percent of original pentosans removed for different times of cooking at concentrations of 25, 50, 75 and 100 grams sodium sulfite per liter of water. The influence of concentration for a given pulp yield was difficult to interpret from these curves. The data were, therefore, replotted in a more useful form. In table 11 are shown the amounts of pentosans removed for different concentrations at certain specific yields (in the high yield range). These data are graphically represented in figure 20. It is clearly seen from this figure that the effect of liquor concentration is quite marked in this yield range. There exists a particular concentration at which the pentosan removal is at a minimum. Rawlings and Staidl have stated (15) that the concentration has no effect on the rate of pentosan removal. This was probably because their work was limited in large measure to yields below 75 percent.

Table 11.--Pentosans Removed for Different Concentrations at 170° C.

Yield	Pentosans removed (percent of original)			
	Sodium sulfite concentration, grams per liter			
	25	50	75	100
Percent	Percent	Percent	Percent	Percent
90	23.0	14.8	12.6	26.4
85	28.7	18.0	20.2	31.5
80	38.0	35.0	32.5	36.7
75	47.5	40.5	41.0	40.5

A similar plotting of lignin values afforded no useful information (table 12). Therefore, in order to get the effect of concentration on lignin removal, curves of the type shown in figure 21 were prepared, where the ratio of pentosan removal to delignification is considered rather than straight pentosan or lignin values. The data for these plots are given in table 13.

Table 12.--Lignin Removed for Different Na_2SO_3 Concentrations at 170° C.

Yield	Lignin removed (percent of original)		
	Sodium sulfite concentration -- grams per liter		
Percent	25	50	75
90	7.3	11.9	9.8
85	14.2	19.3	20.2
80	33.3	36.1	32.6
75	45.9	45.6	44.6

Table 13.--Ratio of Pentosans to Lignin Removed at Different Na_2SO_3 Concentrations at 170° C.

Yield	Ratio of pentosans to lignin removed		
	Sodium sulfite concentration -- grams per liter		
	25	50	75
Percent			
90	2.5	1.24	1.285
85	2.02	.932	.960
80	1.15	.970	1.00
75	.882	.890	.908

It is evident from figure 21 that in the yield range considered, concentrations of less than 50 grams per liter are unfavorable. If one is interested only in the minimum removal of pentosans, a concentration of between 65 and 75 grams per liter is seen to be most desirable (fig. 20). On the other hand, if a maximum delignification is also desired, together with minimum pentosan removal (in the high yield range) a concentration of 50 grams per liter is favored, although higher concentrations will perform equally well.

The results at 220° C. were treated in an identical manner. The variation of yield with concentration is more pronounced in this case (fig. 22). The reversal in pentosan removal that was noticed at 170° C. (fig. 20) is not shown for the total yield at 220° C. Neither is such a reversal shown for the pentosan removal (fig. 23). This absence of reversal either in total yield or pentosan removal can be explained as follows.

Normally, the effect of concentration of the cooking liquor should be uniform either in decreasing the pentosan removal or increasing it. Since pure water removes the pentosans to a greater extent (1) than solutions of sodium sulfite, one would expect that with the increase in sodium sulfite concentration, the loss of pentosans will ~~xixx~~ decrease. It is probable that with an increase in sodium sulfite concentration, two distinct reactions for pentosan removal come into play, viz, salt formation and hydrolysis. In the lower concentration range, as the salt concentration is increased, the excess salt suppresses hydrolysis, thus accounting for a decreased pentosan removal. In this region the rate of salt formation with the uronic acid groups associated with the carbohydrates is very slow, but as the concentration of sodium sulfite is further increased, the rate of salt formation is also increased so that the total pentosan loss once again begins to rise. It should be noted that both these reactions are probably going on in the entire concentration range. But below a certain concentration for a certain temperature, hydrolysis is controlling, while above that concentration salt formation becomes controlling. Since the temperature coefficients of these two reactions are presumably different, it is reasonable to suppose that at a certain temperature salt formation becomes controlling even before the effect of hydrolysis is reduced by increasing sodium sulfite concentration. This accounts for the absence of the minima in the curves of figure 23, the data for which are given in table 14.

Table 14.--Pentosans Removed for Different Na_2SO_3 Concentrations at 220° C.

Yield	Pentosans removed (percent original)		
	Sodium sulfite concentration (grams per liter)		
	12.5	25.0	100
Percent			
90	24.0	21.0	19.0
85	33.0	30.1	25.0
80	42.2	40.0	34.0
75	52.1	48.05	42.0
70	58.9	56.0	49.10

The apparent discrepancy in the constant yield curves for the two temperatures (figs. 20 and 23) is, as pointed out earlier, due to two different reactions that interchange control. The graphical appearance of this effect can be overcome by plotting the ratio of pentosans removed to concentration against yield for the different concentrations. Data for such plots for the two temperatures are given in tables 15 and 16. These are graphically represented in figures 24 and 25. In this method of plotting, the appearance of minima in the curves at 170° C. is avoided. Therefore, while this form is useful for extrapolation and interpolation purposes, it affords no direct information as to the most desirable concentration for a given yield. Considering the curves for 170° C., (fig. 24), from a determination of their slopes, the following equations result:

At a sodium sulfite concentration of 25 grams per liter,

$P = 1.925\ y$;

at a sodium sulfite concentration of 50 grams per liter,

$P = 1.600\ y$;

at a sodium sulfite concentration of 100 grams per liter,

$P = 1.900\ y$;

where P = pentosans removed based on the original content in percent;

and y = yield in percent.

From these equations the presence of an optimum concentration is evident, although this does not show in figure 24.

Table 15.--Ratio of Pentosans Removed to Concentration of Liquor for Different Concentrations in the Yield Range, 70-100% 170° C.

Na_2SO_3 concentration	Pentosans removed -- basis of original	Pentosans removed: concentration	Yield
Gm. per liter	Percent		Percent
25	22.7	0.91	1.10
	28.0	1.12	85
	38.0	1.52	80
	47.5	1.90	75
50	14.00	.28	90
	18.0	.36	85
	34.0	.68	80
	41.0	.82	75
100	26.0	.26	90
	32.0	.32	85
	37.0	.37	80
	41.0	.41	75

Table 16.--<u>Ratio of Pentosans Removed to Concentrations of Liquor for Different Concentrations in the Yield Range 70 to 100 percent, 220° C.</u>

Na_2SO_3 concentration	Pentosans removed -- based on original	Pentosans removed: concentration	Yield
Gm. per liter	Percent		Percent
12.5	24.0	1.92	90
	32.8	2.62	85
	42.0	3.36	80
	52.0	4.16	75
	59.0	4.72	70
25	20.7	.828	90
	30.0	1.20	85
	40.0	1.60	80
	48.0	1.92	75
	55.9	2.24	70
50	18.2	.36	90
	21.8	.44	85
	38.5	.77	80
	44.7	.89	75
	52.0	1.04	70
100	19.0	.190	90
	25.1	.251	85
	34.0	.340	80
	42.5	.425	75
	49.3	.493	70

Mechanism of Pulping

The complex nature of the pulping reactions can be analyzed by considering them as consisting of two main simple reactions, namely,

1. Removal of carbohydrates
2. Removal of noncarbohydrate material (lignin).

The total rate of pulping can then be expressed as the sum of these two rates.

Lignin Removal

The instantaneous rate of removal of lignin may be considered as being dependent upon the instantaneous fraction of lignin present and its availability. The availability of the lignin depends upon the instantaneous pulp content and is hence dependent upon both the lignin and total carbohydrate present. This rate of delignification can be expressed by the equation

$r_1 = k_1$ (availability of lignin) (amount of lignin present).

This can be expressed as

$$r_1 = k_1 \left[1 - \alpha_1 (x_1 + x_2) \right] x_1 = - \frac{dx_1}{dt} \quad \text{---------------(1)}$$

where

r_1 = rate of lignin removal (grams of lignin per gram of wood per minute),

x_1 = grams of residual lignin per gram of wood,

x_2 = grams of residual carbohydrates per gram of wood,

k_1 = reaction velocity constant,

α_1 = a constant, depending upon nature of wood.

Since all the graphs are in terms of original amount of lignin present in the wood, equation (1) can be modified to be directly applicable.

Let

c_1 = grams of initial lignin per gram of wood

f_1 = fraction of lignin removed

$$\frac{c_1 - x_1}{c_1} = f_1$$

$$x_1 = c_1(1 - f_1) \quad \text{--------------------------}(2)$$

From equations (1) and (2), equations (3) and (4) result.

$$r_1 = k_1 \left[1 - \alpha_1 \quad (c_1 + c_2) - (c_1 f_1 + c_2 f_2) \right]$$

$$c_1(1 - f_1) \quad \text{---------}(3)$$

or

$$r_1 = k_1 \left[1 - \alpha_1 (1 - c_1 f_1 - c_2 f_2) \; c_1(1 - f_1) \right]$$

$$= - \frac{dx_1}{dt} \quad \text{---------}(4)$$

α_1 and k_1 can be evaluated by determining r_1 for any two values of pulp yield at a given temperature. With this value of α_1, k_1 for other temperatures can be evaluated.

<u>Sample Calculation</u>

210° C.

At 90 percent yield, $f_1 = 0.11$, $f_2 = 0.05$, $c_1 = 0.285$, and $c_2 = 0.715$.

Then,

$$r = - \frac{dx}{dt} = - 0.0435 = k_1 \left[1 - \alpha_1 (1 - 0.0308 - 0.0357) \right] (0.254)$$

or

$$- 0.171 = k_1(1 - 0.9335\alpha_1).$$

At 75 percent yield

$$- 0.0174 = k_1 \left[1 - \alpha_1(1 - 0.128 - 0.1265)\right] 0.157$$

or

$$- 0.11060 = k_1(1 - 0.7455\ _1).$$

Hence,

$$k_1 = 0.129$$

$$\alpha_1 = 2.49.$$

Similar calculations were made for 200° C. and 220° C. in the yield range 70-100 percent. The results are given in table 17.

Carbohydrate Removal

The instantaneous rate of removal of carbohydrates may be considered as being dependent upon the instantaneous fraction of carbohydrates present and their availability. The availability of the carbohydrates, as in the case of lignin, depends upon the instantaneous pulp content and hence upon the lignin and total carbohydrates present. This rate of carbohydrate removal can be expressed by the equation

$$r_2 = k_2 \left[1 - \alpha_2 (x_1 + x_2)\right] x_2$$

where k_2 = reaction velocity constant,

α_2 = a constant depending upon nature of wood.

Calculations similar to those for lignin removal were made.

$$\alpha_2 = 1.54$$

Values of k_2 are shown in table 17.

Table 17.

Temperature (°C.)	k_1	k_2
200	0.084	0.110
210	0.129	0.168
220	0.107	0.215

Using the Arrhenius equation for the effect of temperature on reaction velocity constant (figs. 26 and 27), k_1 and k_2 are expressed as follows:

$$k_1 = (1.1)(10)^6 \; e^{\left(-\frac{15,300}{RT}\right)} \quad \text{-------------}(5)$$

$$k_2 = (2.42)\, 10^6 \, e^{\left(-\frac{15,800}{RT}\right)} \quad \text{-------------}(6)$$

Hence the final equations are:

Lignin

$$r_1 = -\frac{dx_1}{dt} = (1.1)(10^6)\, e^{\left(-\frac{15,300}{RT}\right)} \; 1 - 2.49\, (x_1 = x_2)\, x_1 \text{---}(7)$$

Carbohydrates

$$r_2 = -\frac{dx_2}{dt} = (2.42)(10^6)\, e^{\left(-\frac{15,800}{RT}\right)} \; 1 - 1.54\, (x_1 = x_2)\, x_2 \text{---}(8)$$

$$r = r_1 = r_2 \quad \text{-------------------------------}(9)$$

Values of r_1 and r_2 calculated from equations (7) and (8) were compared with experimental values. In table 18 are shown the values for 200° C. The agreement between the experimental and calculated values is seen to be (table 19) very close (figs. 28 and 29). Experimentally obtained pulping rates were compared with the rates obtained from equation (9). Here again the agreement is close (fig. 30). Percent deviations for different yields are also tabulated (table 19). The deviations are small enough to warrant recommendation of equations (7), (8), and (9) for the yield range 70-100 percent.

Table 18.--Comparison of Calculated and Experimental Rates at 200° C.

Yield	Rate of lignin removal		Rate of carbohydrate removal		Total pulping rate	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
Percent						
90	0.0248	0.0256	0.0286	0.0295	0.0534	0.0537
80	0.0138	0.0157	0.0146	0.0147	0.0284	0.0274
75	0.00965	0.00941	0.00772	0.0075	0.01737	0.0154
70	0.00177	0.00153	0.00246	0.00187	0.00423	0.00429

Table 19.--Percent Deviation if Calculated From Experimental Rates

Yield	Percent deviation		
	Lignin removal	Pentosan removal	Pulp yield
Percent			
90	-3.2	-3.05	-0.57
80	-12.0	-0.67	+3.65
75	+2.55	+2.85	+13.0
70	+16.1	....	-1.4

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APPENDIX

Series 1.--Effect of temperature on the yield of pulp and pulp fractions.

Series 1.--Effect of temperature on the yield of pulp and pulp fractions.

Aspen Sawdust (20-40 Mesh) Cooked With Na_2SO_3 Solutions (50 grams per liter) With a Liquor-wood Ratio of 40

Time	Amounts present (based on original wood)												Amounts removed (based on original amounts in wood)								
	Temperature (°C.)												Temperature (°C.)								
	Yield (Percent)			Total carbohydrates (Percent)			Lignin (Percent)			Pentosans (Percent)			Total carbohydrates (Percent)			Lignin (Percent)			Pentosans (Percent)		
	200	210	220	200	210	220	200	210	220	200	210	220	200	210	220	200	210	220	200	210	220
Min.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
1	91.0	88.1	86.0	67.5	62.3	65.7	23.5	20.2	20.3	19.0	15.58	16.45	5.05	14.0	9.5	13.5	26.6	26.1	15.4	30.7	28.4
2	86.3	......	80.3	65.9	61.05	60.5	20.4	15.8	19.8	17.5	13.26	12.45	9.2	15.7	16.6	24.6	42.6	28.1	22.5	41.0	45.8
5	81.1	72.8	63.5	65.1	60.2	52.4	16.0	8.6	11.1	14.0	12.15	10.70	15.7	16.9	27.4	41.7	68.4	59.6	35.2	46.0	61.0
10	71.3	67.6	59.6	58.8	57.9	50.0	12.5	9.7	9.6	13.6	11.33	5.54	18.9	20.2	31.2	54.7	64.8	65.1	39.5	49.7	75.9
15	72.0	......	60.01	....	54.1	....	12.2	......	....	13.5	....	....	....	25.4	......	55.6	......	......	40.0	......	......
20	69.8	62.0	50.7	57.9	53.85	46.6	11.9	7.4	4.1	13.1	10.32	5.53	22.5	25.8	36.8	56.2	73.1	85.1	41.6	54.2	76.1
	150	170	190	150	170	190	150	170	190	150	170	190	150	170	190	150	170	190	150	170	190
2	......	94.1	89.5	....	69.0	64.0	......	25.1	25.5	......	19.0	18.1	....	4.4	10.5	......	11.9	10.5	......	16.1	20.5
5	89.5	89.5	85.1	68.5	66.5	....	20.8	23.0	18.6	21.05	18.8	16.5	4.2	7.0	......	......	19.3	34.7	7.2	17.0	27.5
15	87.4	85.7	76.3	67.2	65.5	60.5	20.2	18.2	15.8	20.5	18.34	15.8	5.9	8.5	15.2	......	36.1	44.9	9.7	19.0	30.0
30	87.5	83.0	74.7	66.8	64.6	57.1	19.3	18.4	17.6	20.4	17.7	14.12	6.5	9.6	20.1	......	35.3	38.3	9.9	32.0	37.7
45	......	......	....	....	....	....	18.9	......	......	......	....	....	7.6	......	24.0	......	......	43.8	......	......	......
60	87.1	80.3	70.3	66.0	62.3	54.3	......	18.0	16.2	20.15	14.1	10.72	....	12.8	24.0	......	36.8	43.1	10.5	37.9	52.8
90	87.0	78.8	68.1	....	62.0	52.0	22.3	16,8	16.1	......	13.94	10.55	8.8	13.4	27.2	......	41.1	43.3	......	38.8	53.6
120	87.0	75.5	64.0	63.4	60.0	50.75	24.1	15.5	13.25	19.67	13.45	10.17	11.3	16.1	28.9	......	45.6	53.4	13.3	40.8	55.3

Analysis of uncooked sample (aspen sawdust)

1. Total carbohydrates:..... 71.5 percent
2. Non-carbohydrate material (referred to as lignin): 28.5 percent
3. Pentosans:.............. 22.7 percent

Series 2.--Effect of sodium sulfite concentration on the yield of pulp and pulp fractions.

Effect of Sodium Sulfite Concentration on Yield of Pulp and Pulp Fractions at 220° C.

Time	Sodium sulfite concentration															
	Yield (Percent)				Total carbohydrates removed[1] (Percent)				Lignin removed[1] (Percent)				Pentosans removed[1] (Percent)			
	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100	12.5	25	50	100
Min.	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter
1	84.7	87.0	86.0	76.7	11.5	8.4	9.5	13.0	25.0	25.5	26.1	50.9	31.7	26.7	28.4	35.5
2	80.5	80.5	80.3	73.05	19.4	17.7	16.6	18.5	20.2	24.8	28.1	49.5	44.2	48.5	45.8	47.0
5	62.2	64.5	63.5	56.4	26.2	27.8	25.4	26.8	....	62.5	59.6	88.1	62.0	....	61.0	61.1
10	60.1	60.5	59.6	52.7	30.2	29.2	31.2	31.2	63.5	67.0	65.1	90.3	77.2	77.2	75.9	....
20	56.7	56.0	50.7	46.0	....	32.2	35.8	38.7	73.1	74.9	85.1	94.5	75.3	76.0	76.1	76.1

Effect of Sodium Sulfite Concentration on Yield of Pulp and Pulp Fractions at 170° C.

	25	50	75	100	25	50	75	100	25	50	75	100	25	50	75	100
	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter	Gm. per liter
2	94.1	94.1	94.0	94.3	68.3	69.0	68.3	....	9.2	11.9	9.8	....	23.0	16.2	12.6	26.4
5	88.0	89.5	89.0	87.3	63.5	66.4	65.2	....	14.2	19.3	20.2	....	29.2	17.0	....	31.2
15	81.7	85.7	84.3	85.6	62.8	65.1	65.1	....	33.3	36.1	29.0	....	35.3	....	24.0	32.2
30	81.9	83.0	82.6	86.1	62.8	64.6	67.3	....	32.7	35.3	34.0	....	35.3	32.0	28.4	34.4
60	80.9	80.3	81.0	86.1	62.5	62.3	69.3	....	35.5	36.8	41.0	....	35.6	37.9	....	39.2
120	75.0	74.5	75.4	75.6	59.55	60.0	59.8	....	45.9	45.6	44.6	....	39.6	40.8	40.3	....

---

[1] Based on original amount present.

M 89243 F

Series 3.--Effect of liquor-wood ratio on the yield of pulp and pulp fractions.

Effect of Liquor-wood Ratio on the Yield of Pulp and Pulp Fractions at 170° C.

Time	Liquor to wood ratio															
	Yield (Percent)				Amounts removed (based on original amounts in wood)											
					Total carbohydrates (Percent)				Lignin (Percent)				Pentosans (Percent)			
	10	20	40	80	10	20	40	80	10	20	40	80	10	20	40	80
Min.																
2	94.5	94.3	94.1	90.3	4.3	......	4.4	4.6	9.9	......	11.9	......	4.8	10.9	16.1	18.1
5	89.6	89.4	89.5	86.7	4.8	......	7.0	7.5	17.1	......	19.3	27.7	12.0	16.2	17.0	17.8
15	85.7	85.8	85.7	82.7	7.2	7.28	8.5	8.9	32.6	31.6	36.1	38.0	15.8	20.1	19.0	19.8
30	85.5	84.6	83.0	83.0	8.0	8.7	9.6	10.4	30.2	31.6	35.3	34.5	18.9	......	32.0	34.7
60	81.4	81.8	80.3	80.1	8.5	10.5	12.8	13.2	43.9	37.5	36.8	35.9	23.7	26.6	37.9	42.1
120	79.7	80.2	74.5	73.8	9.5	11.7	13.4	14.5	47.5	40.4	45.6	55.8	23.7	35.5	40.8	42.8

M 89244 F

Plate 1.--Pressure autoclave

Plate 2.--Molten salt bath with the reactor holder.

Plate 3.--High temperature reactor

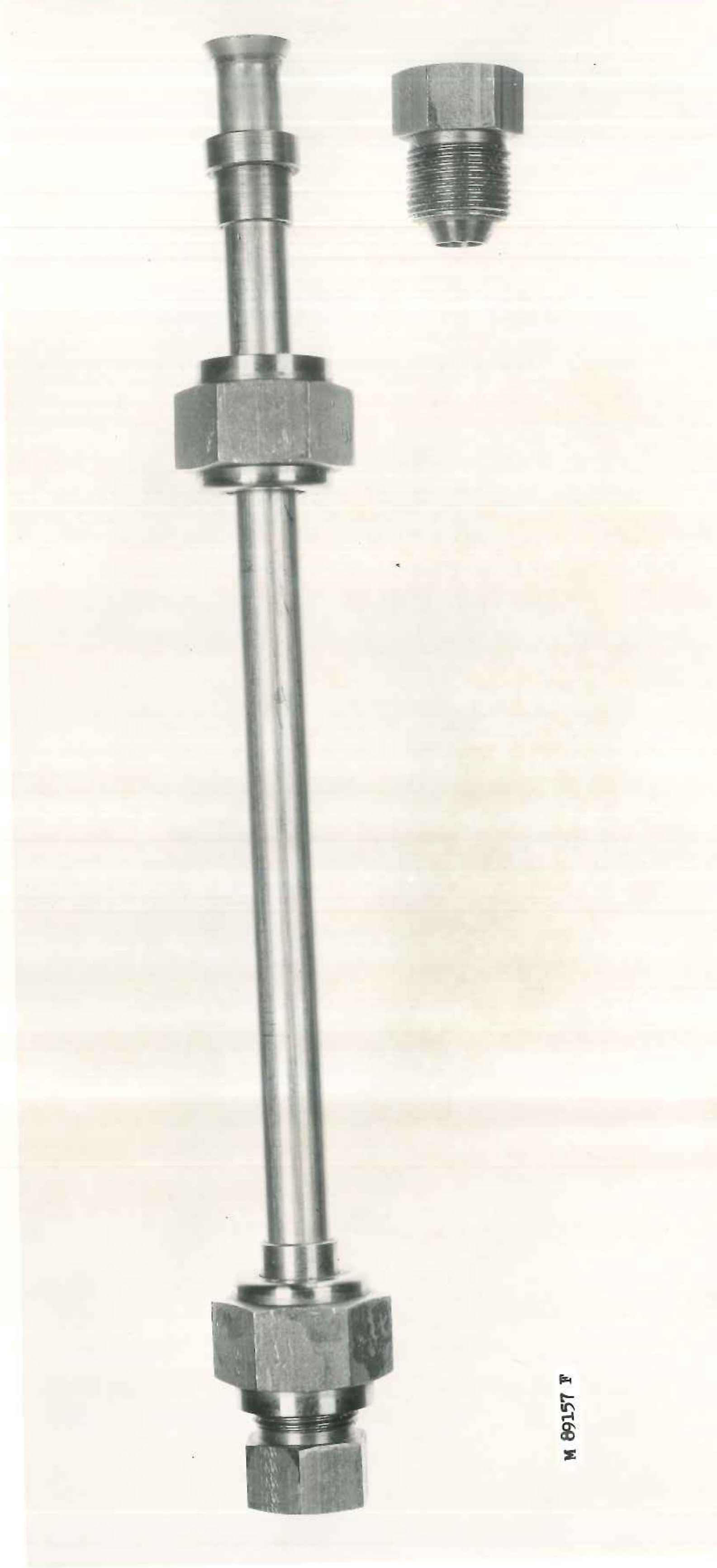
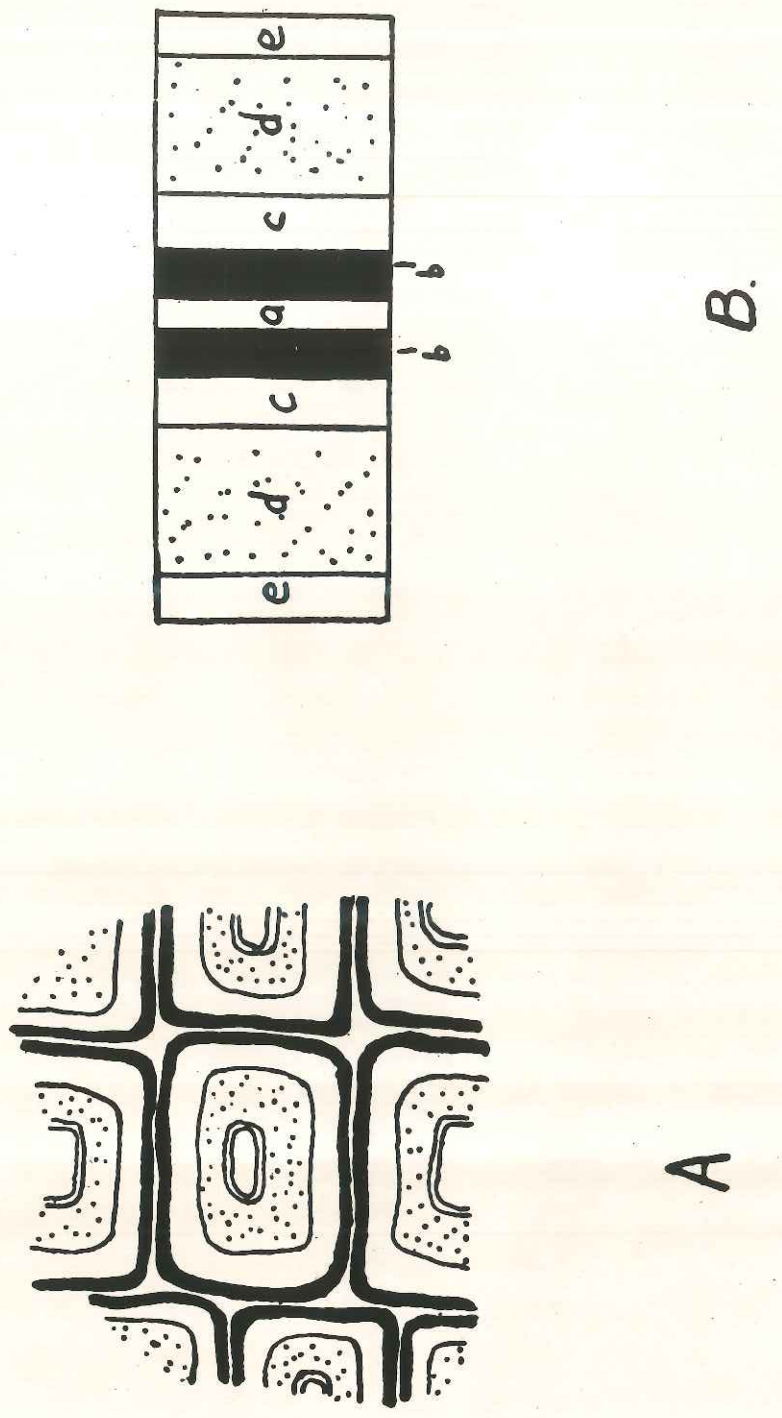


Plate 4.--Wood structure

Bixler (5)

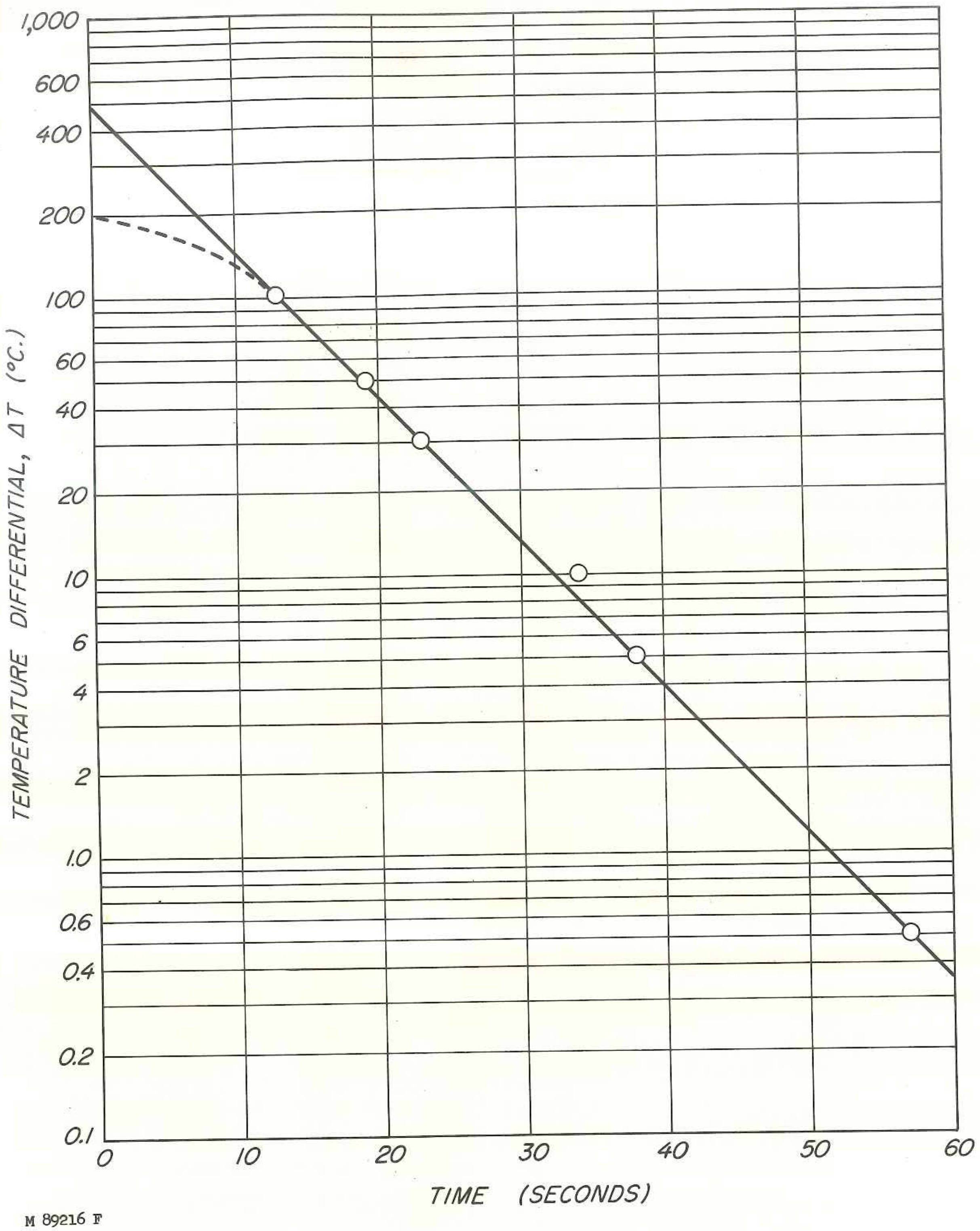
Kerr and Bailey (12)



A. Diagram of a transverse section of a tracheid (*10*). B. Section of adjacent walls (*10*). a. Truly isotropic intercellular material. b. Cambial or primary wall. c. Outer layer of secondary wall. d. Central layer of secondary wall. e. Inner layer of secondary wall.

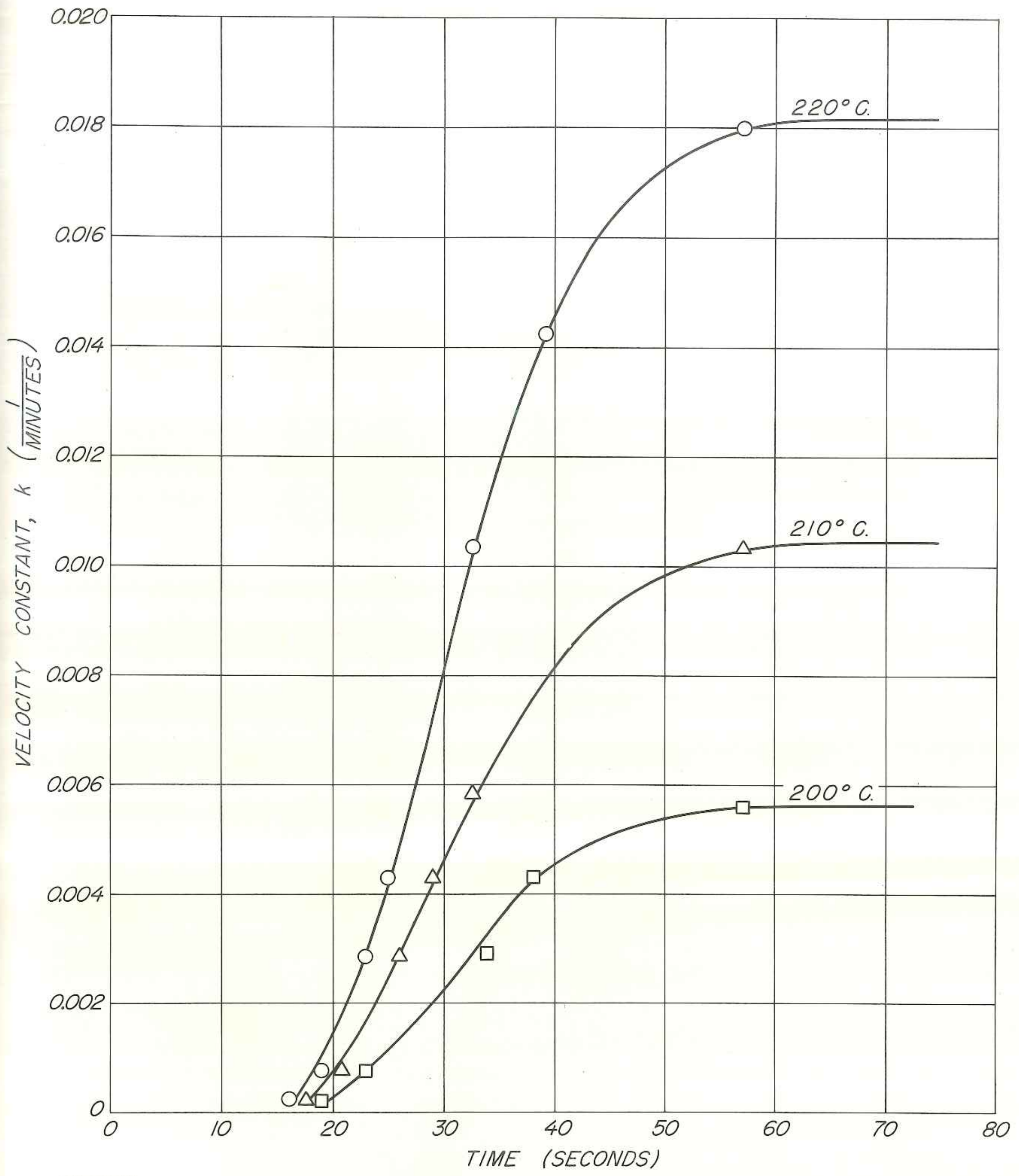
M 89181 F

Figure 1.--Time for heating the reactor to 200° C. by temperature intervals, ΔT



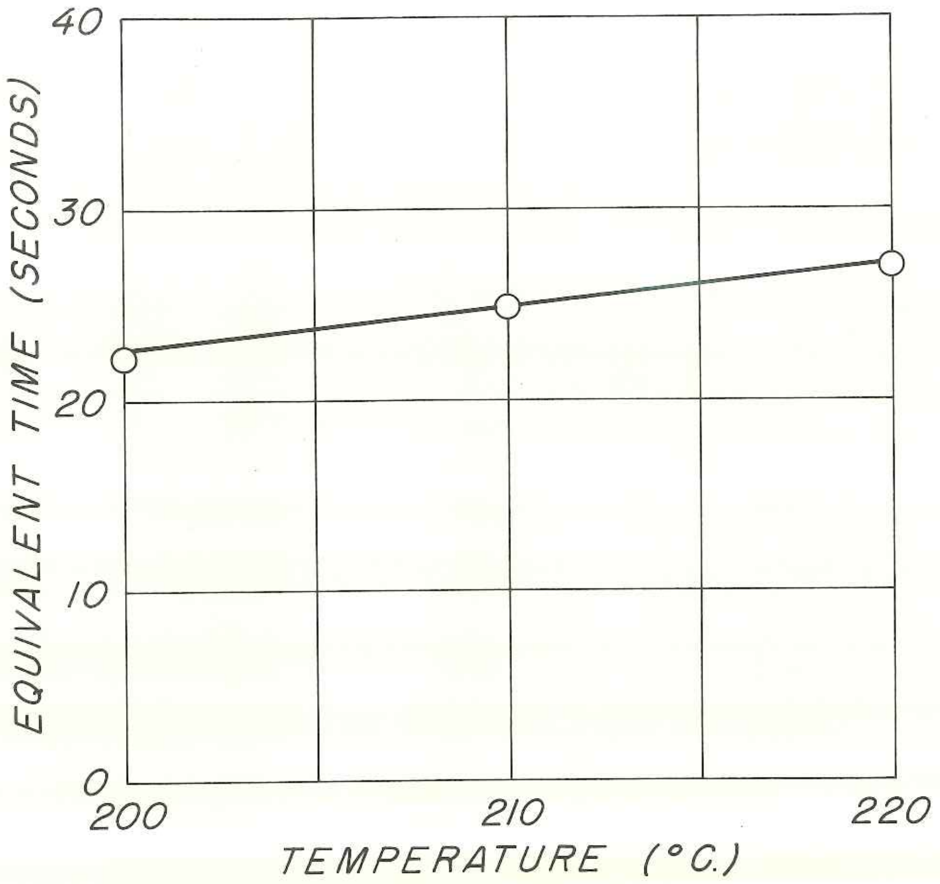
M 89216 F

Figure 2.--Velocity constants for different reactor temperatures plotted against the corresponding times required during the initial heating period.



M 89222 F

Figure 3.--Equivalent times for different final temperatures.



M 89217 F

Figure 4.--Total yield (percent based on original oven-dried wood) plotted against time for various temperatures.

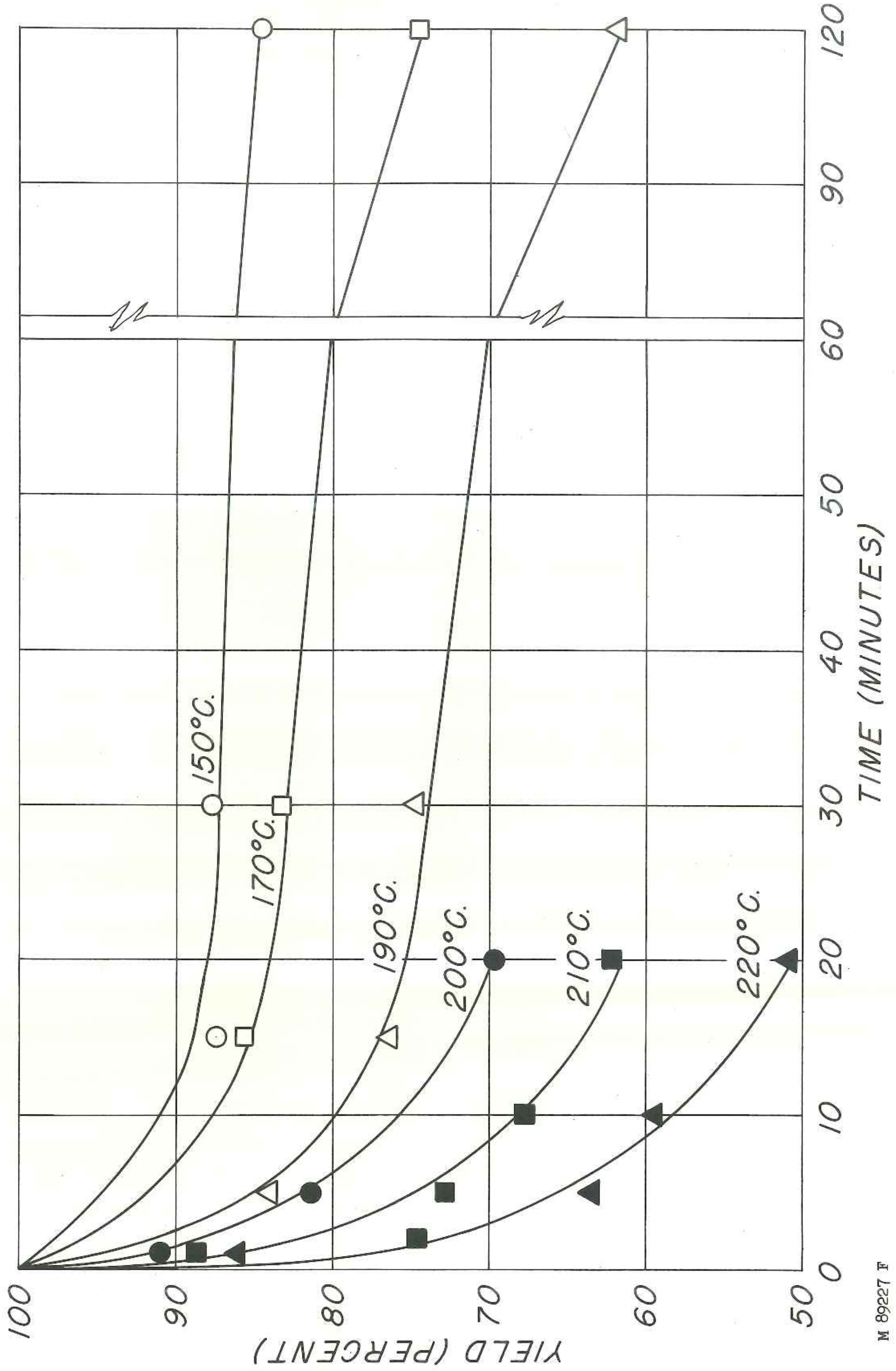
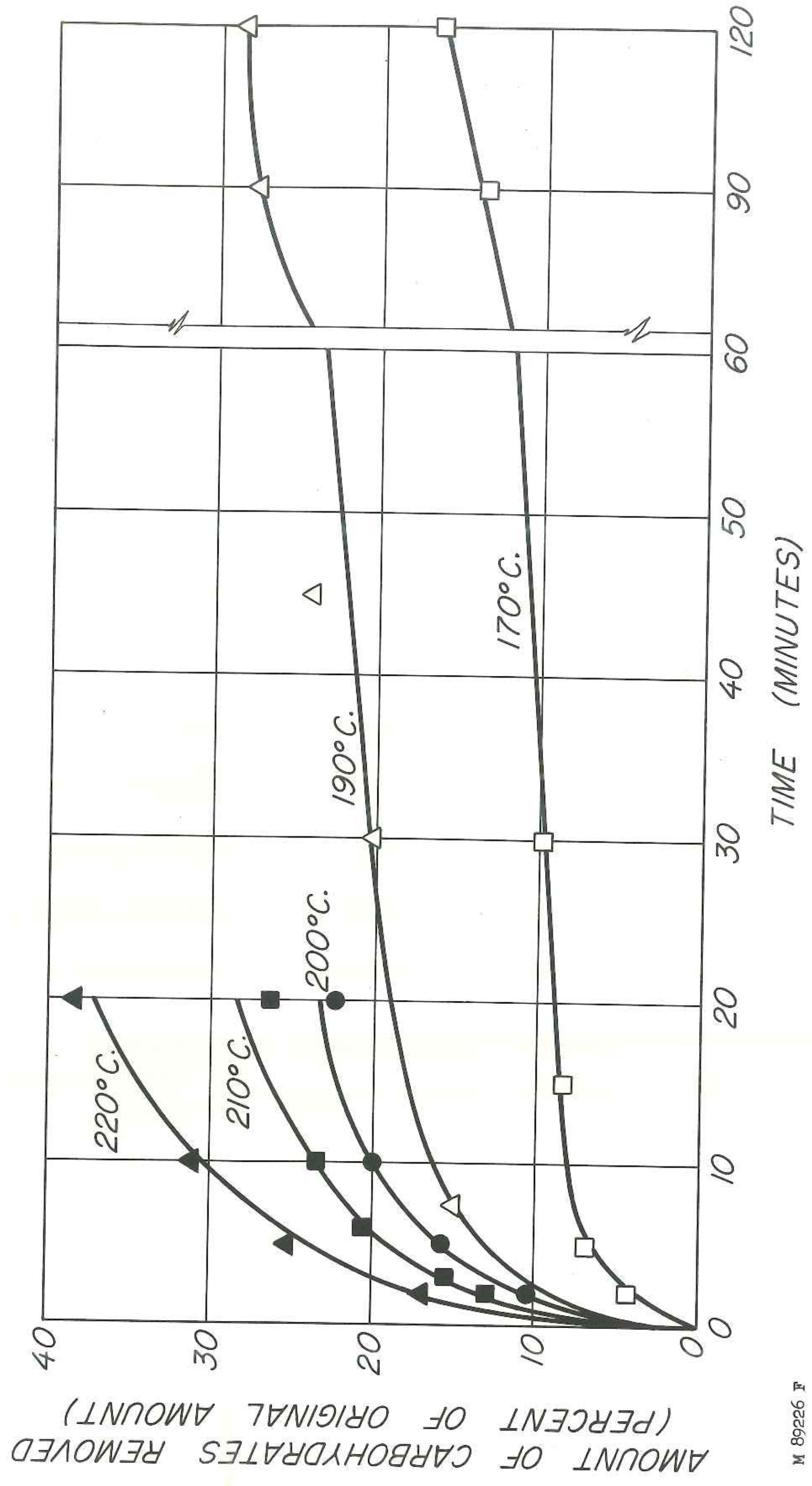
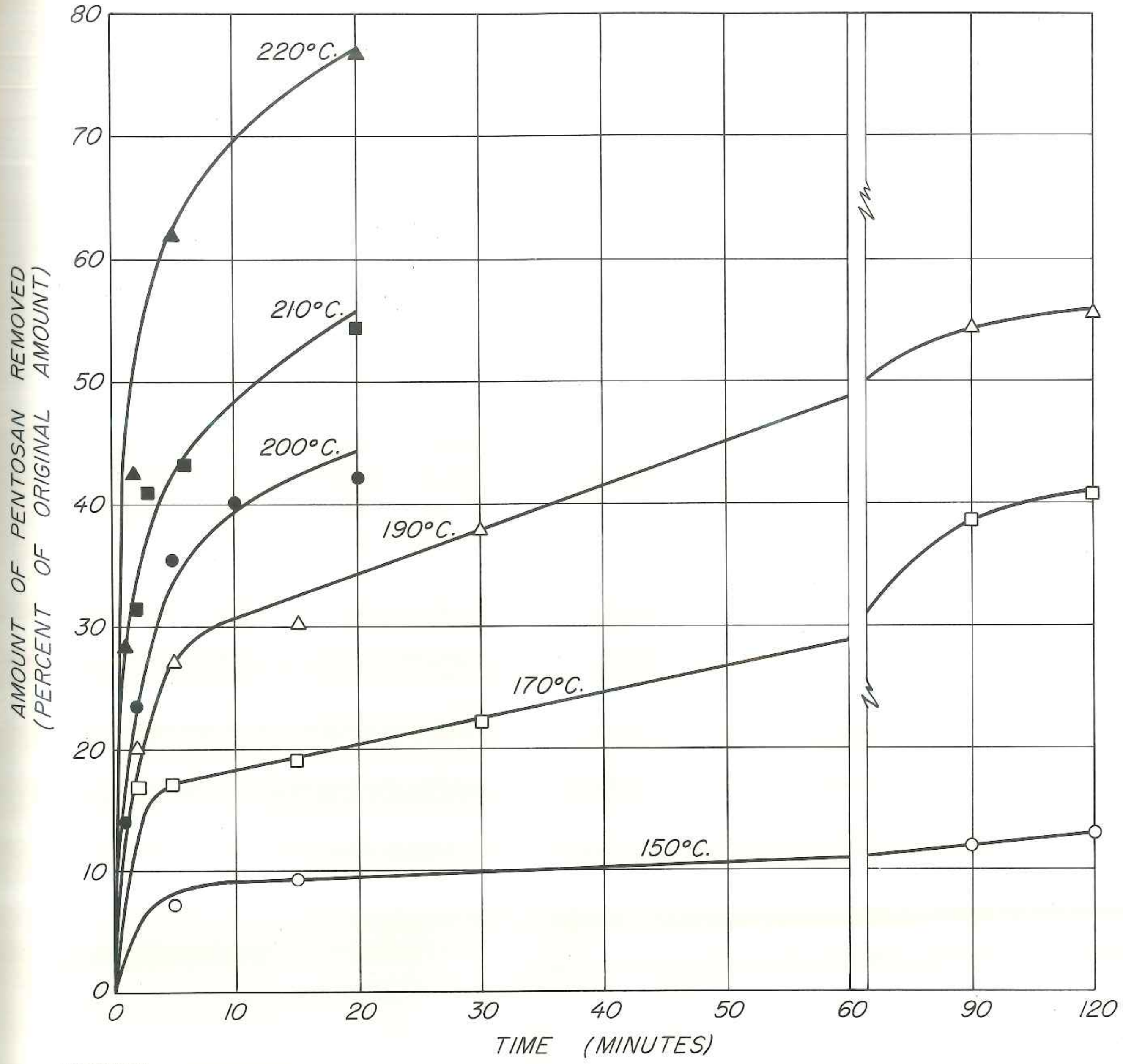


Figure 5.--Total carbohydrate removal (percent of original carbohydrates present in wood) plotted against time for various temperatures.



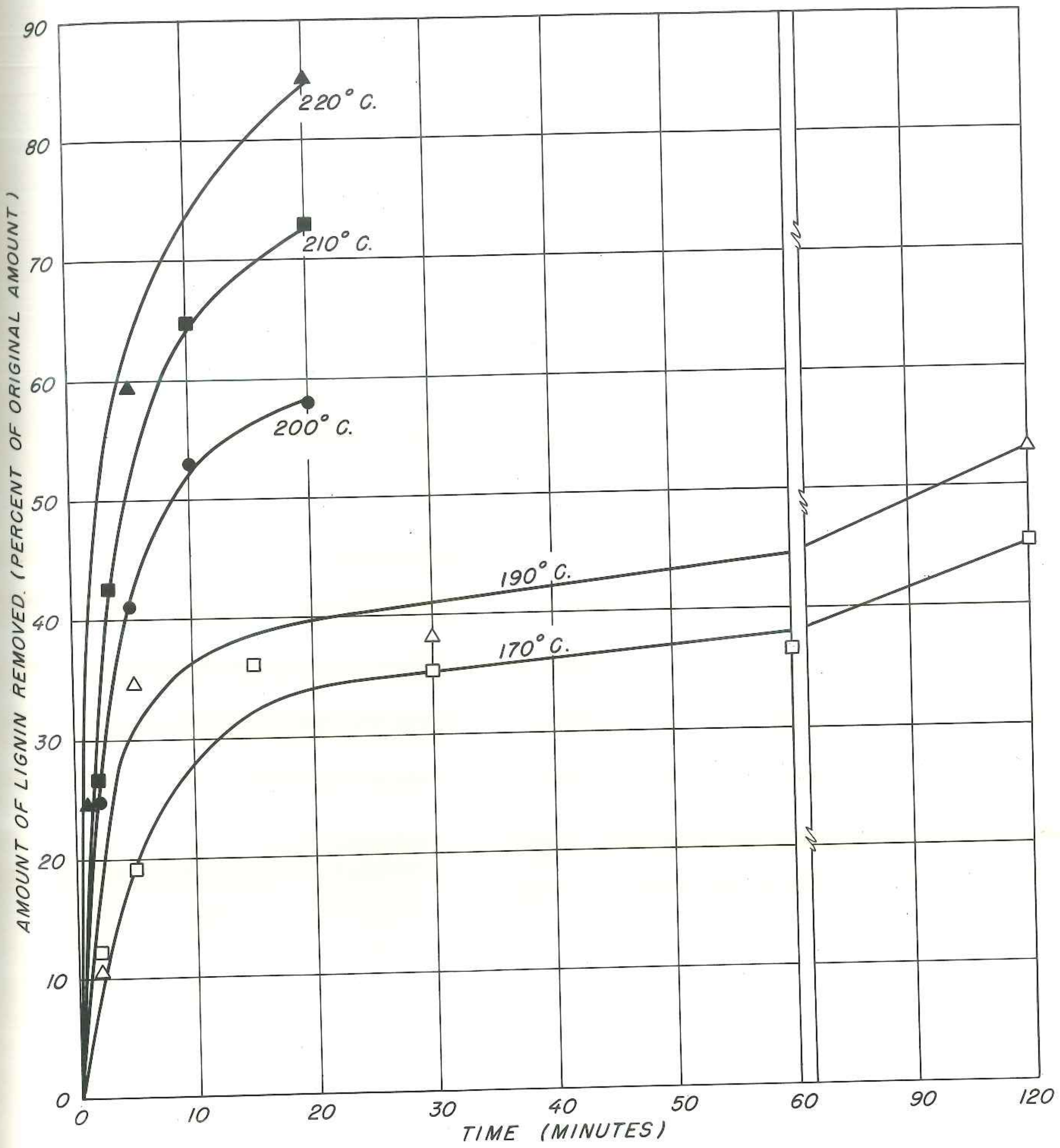
M 89226 F

Figure 6.--Pentosan removal (percent of original pentosans present in wood) plotted against time for various temperatures.



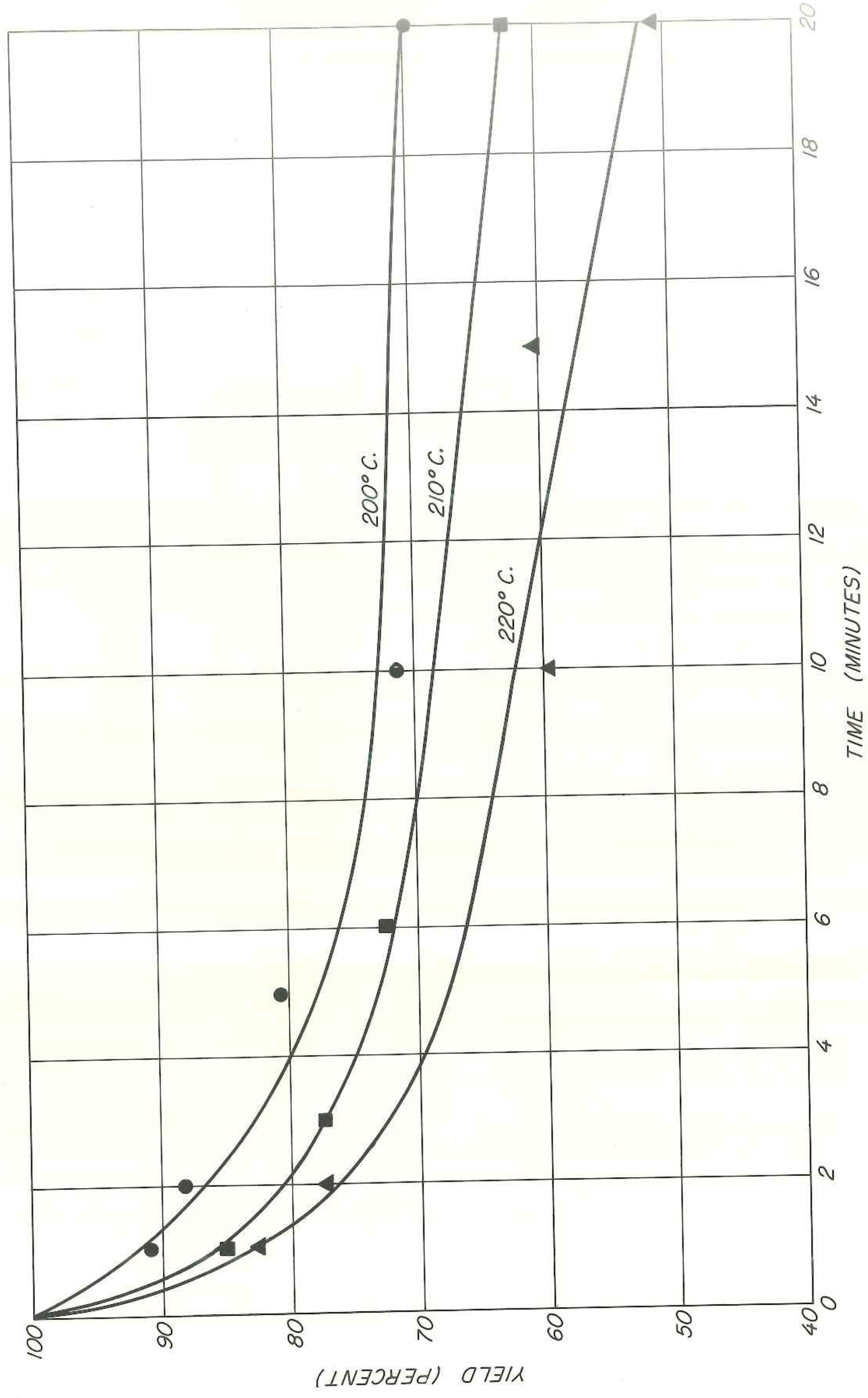
M 89224 F

Figure 7.--Lignin removal (percent of original lignin present in wood) plotted against time for various temperatures.



M 89228 F

Figure 8.--Total yield (percent based on original oven-dried wood) plotted against time at 200° C., 210° C., and 220° C.



M 89240 F

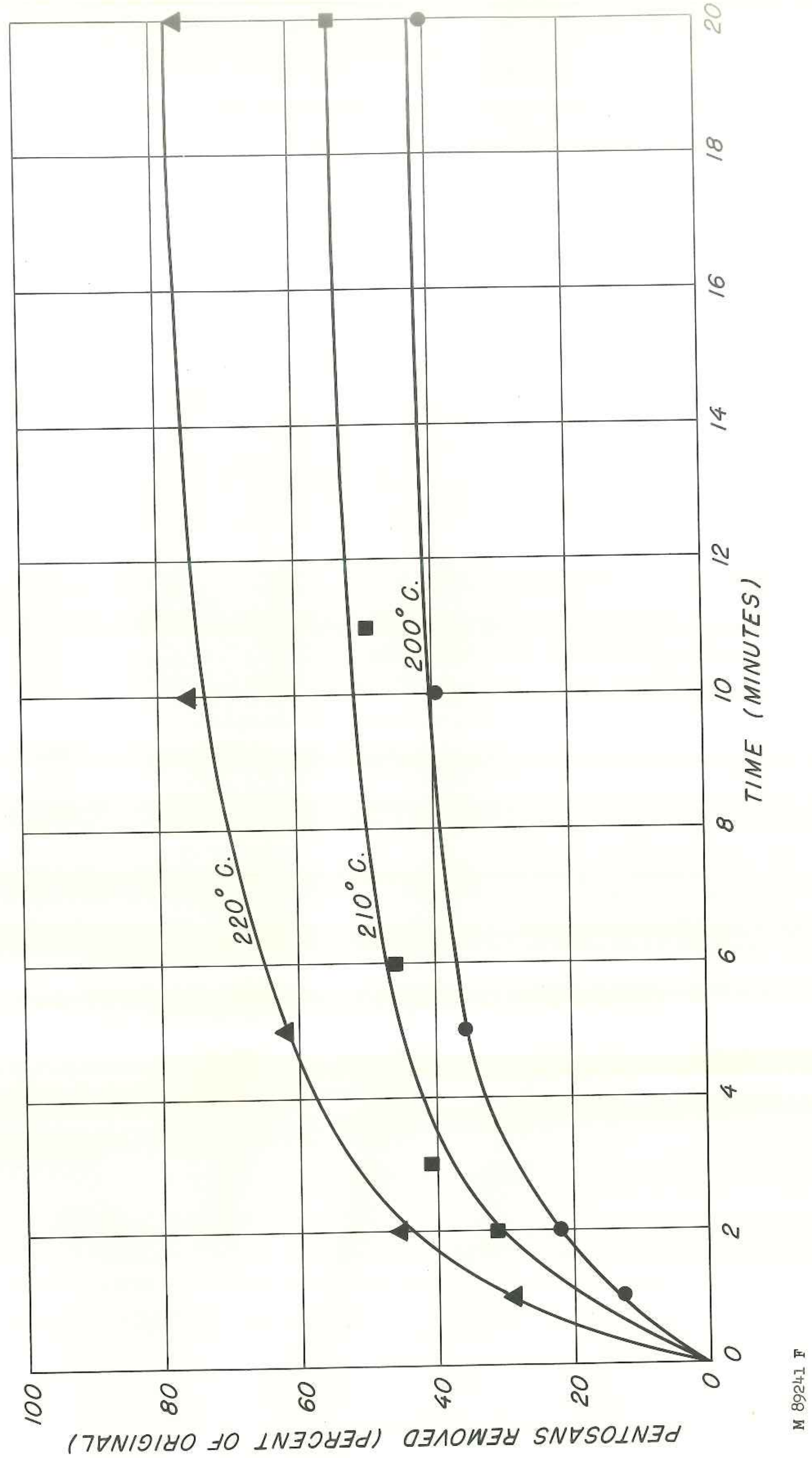
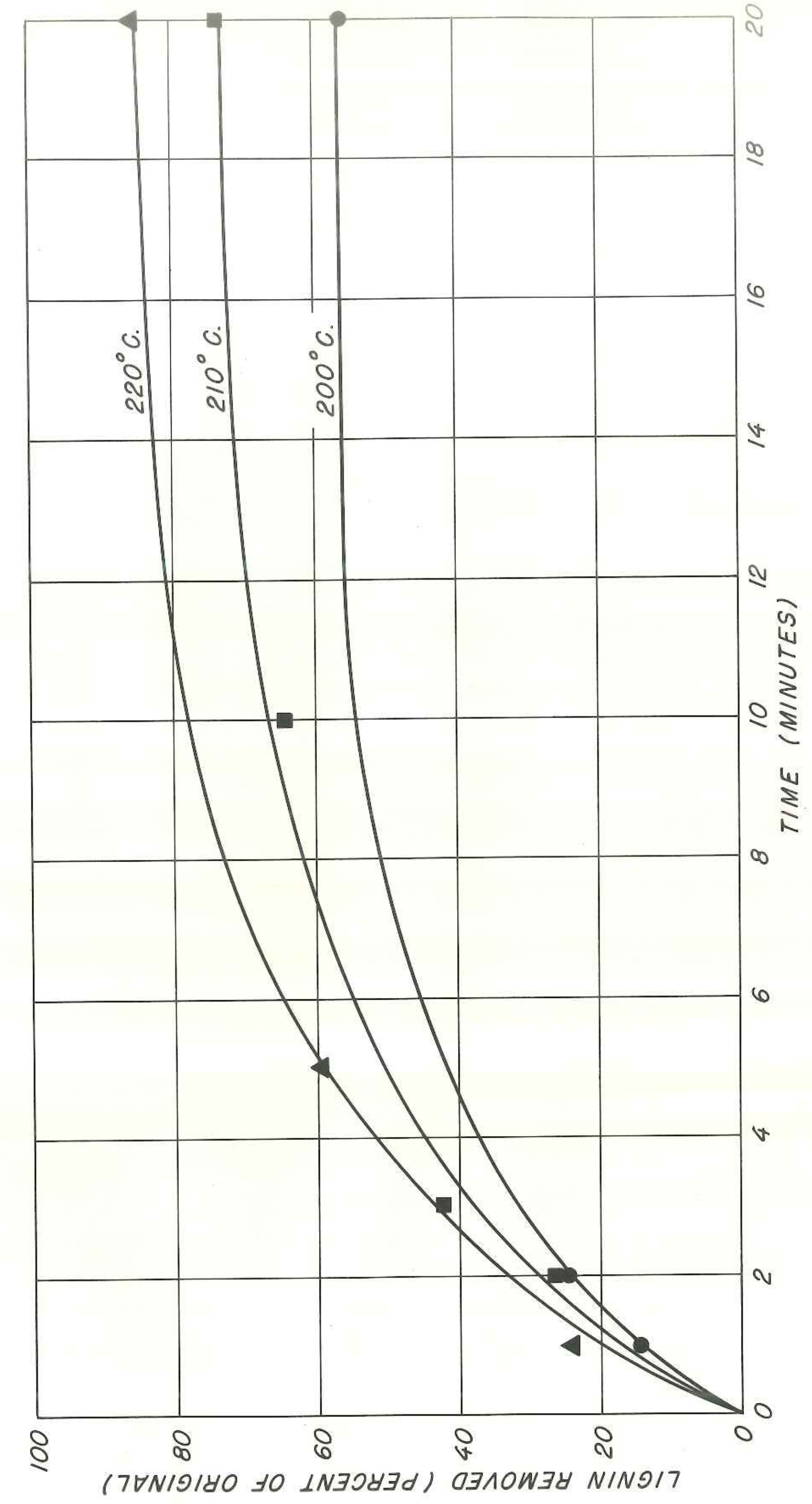


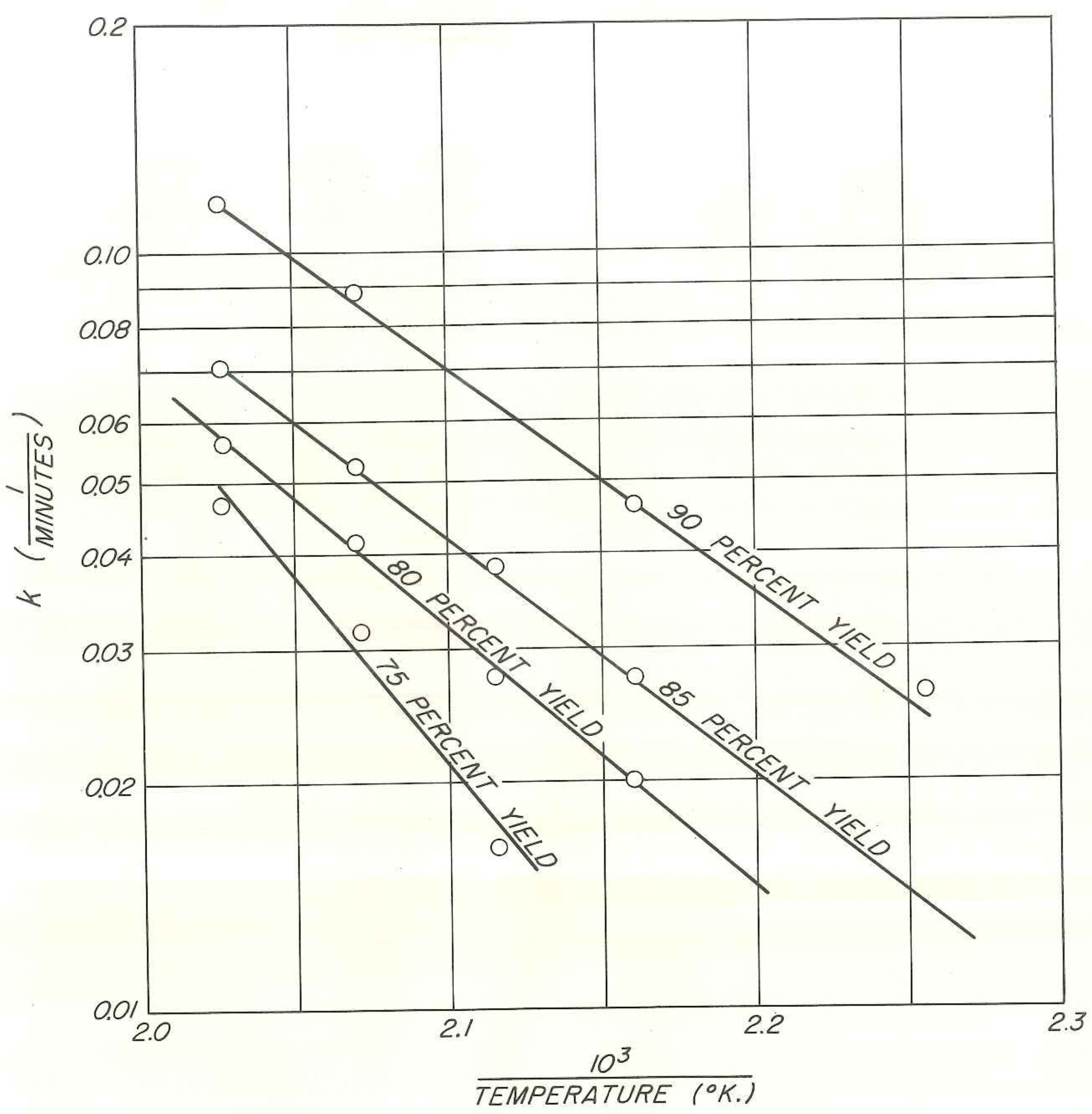
Figure 9.--Pentosan removal (percent of original pentosans present in wood) plotted against time at 200° C., 210° C., and 220° C.

Figure 10.--Lignin removal (percent of original lignin present in wood) plotted against time at 200° C., 210° C., and 220° C.



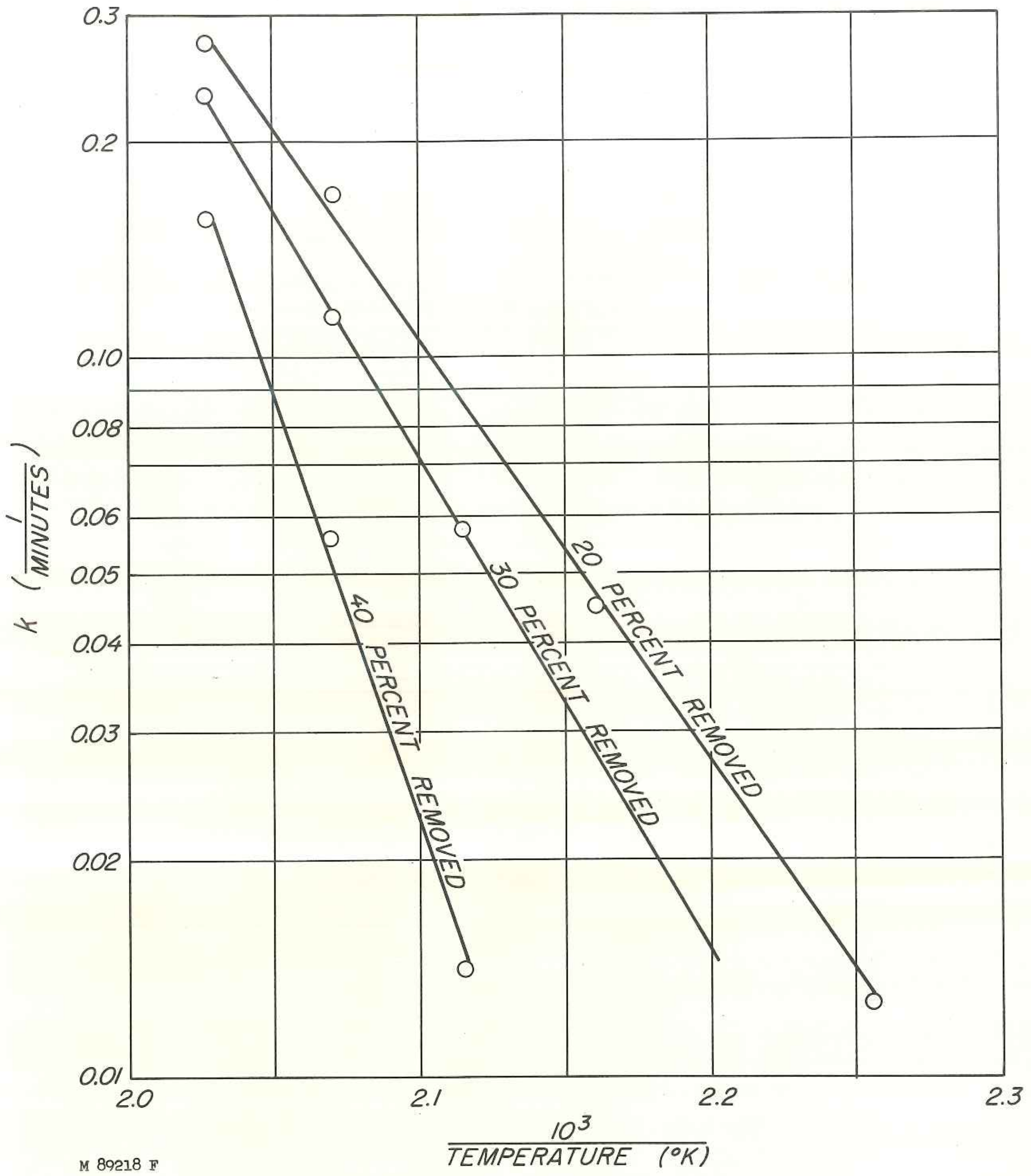
M 89239 F

Figure 11.--Reaction velocity constants plotted against reciprocal absolute temperatures for various parameters of constant yield.



M 89214 F

Figure 12.--Reaction velocity constants plotted against reciprocal absolute temperatures for various percentages of pentosan removal.



M 89218 F

Figure 13.--Reaction velocity constants plotted against reciprocal absolute temperatures for various percentages of lignin removal.

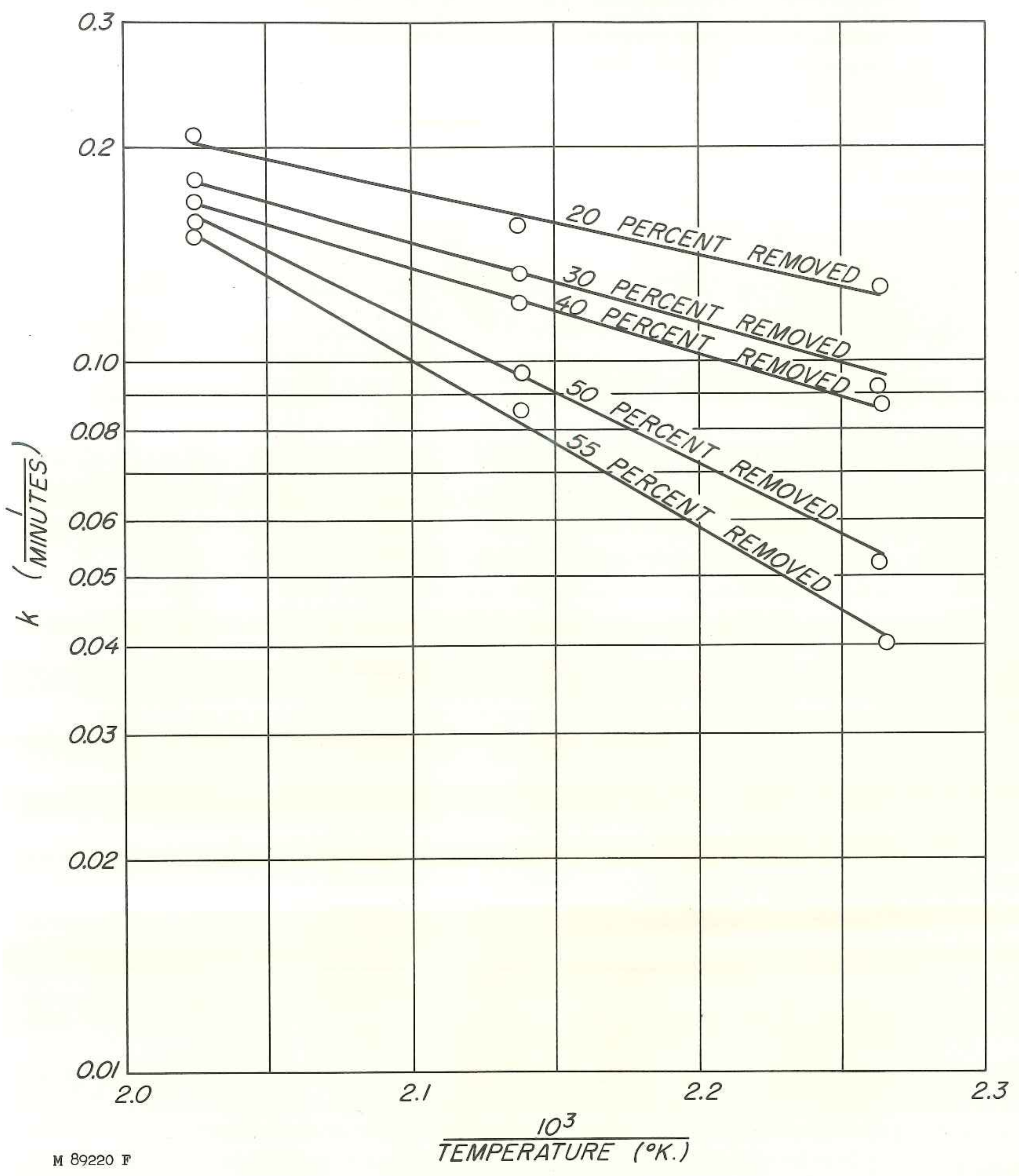
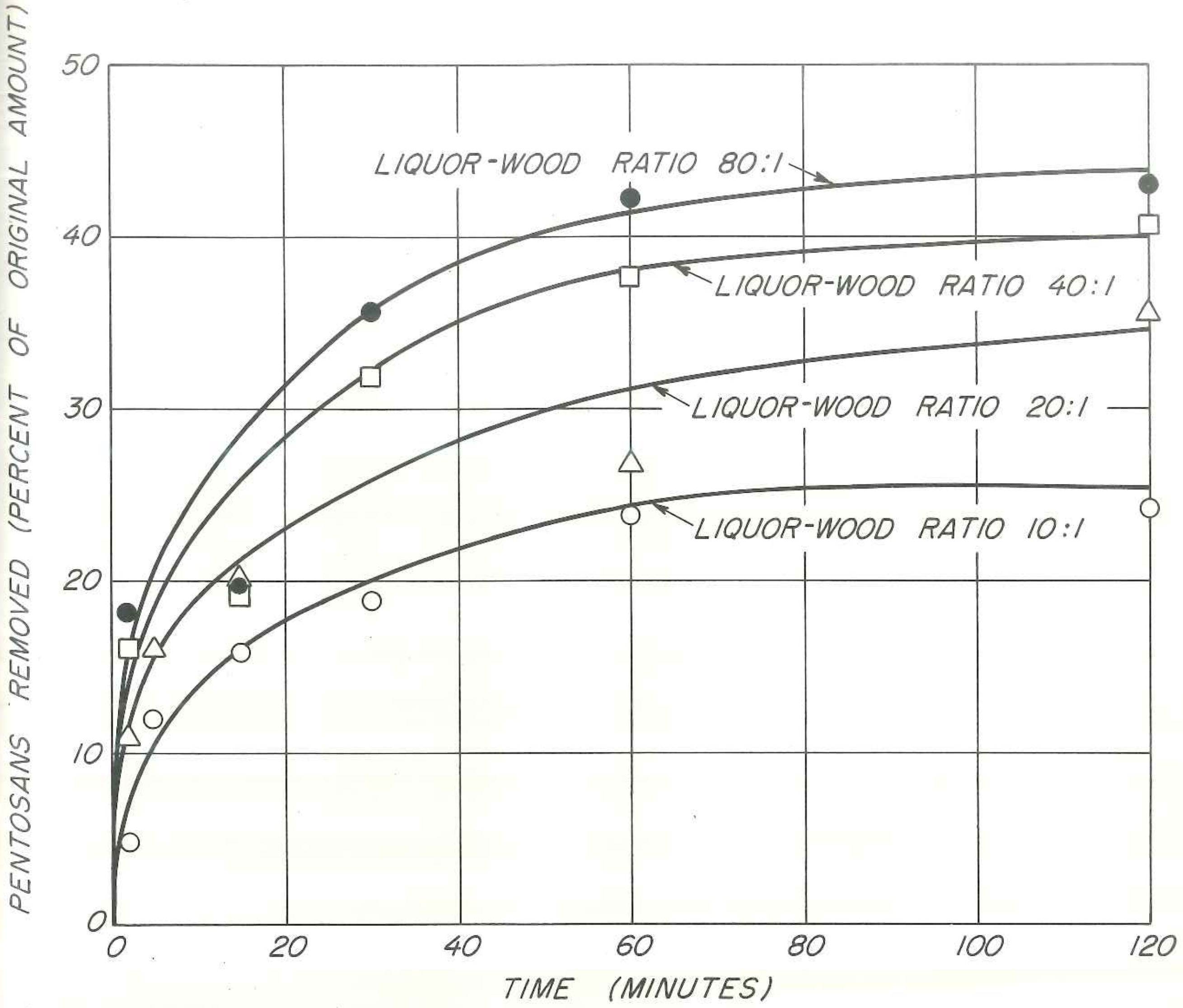
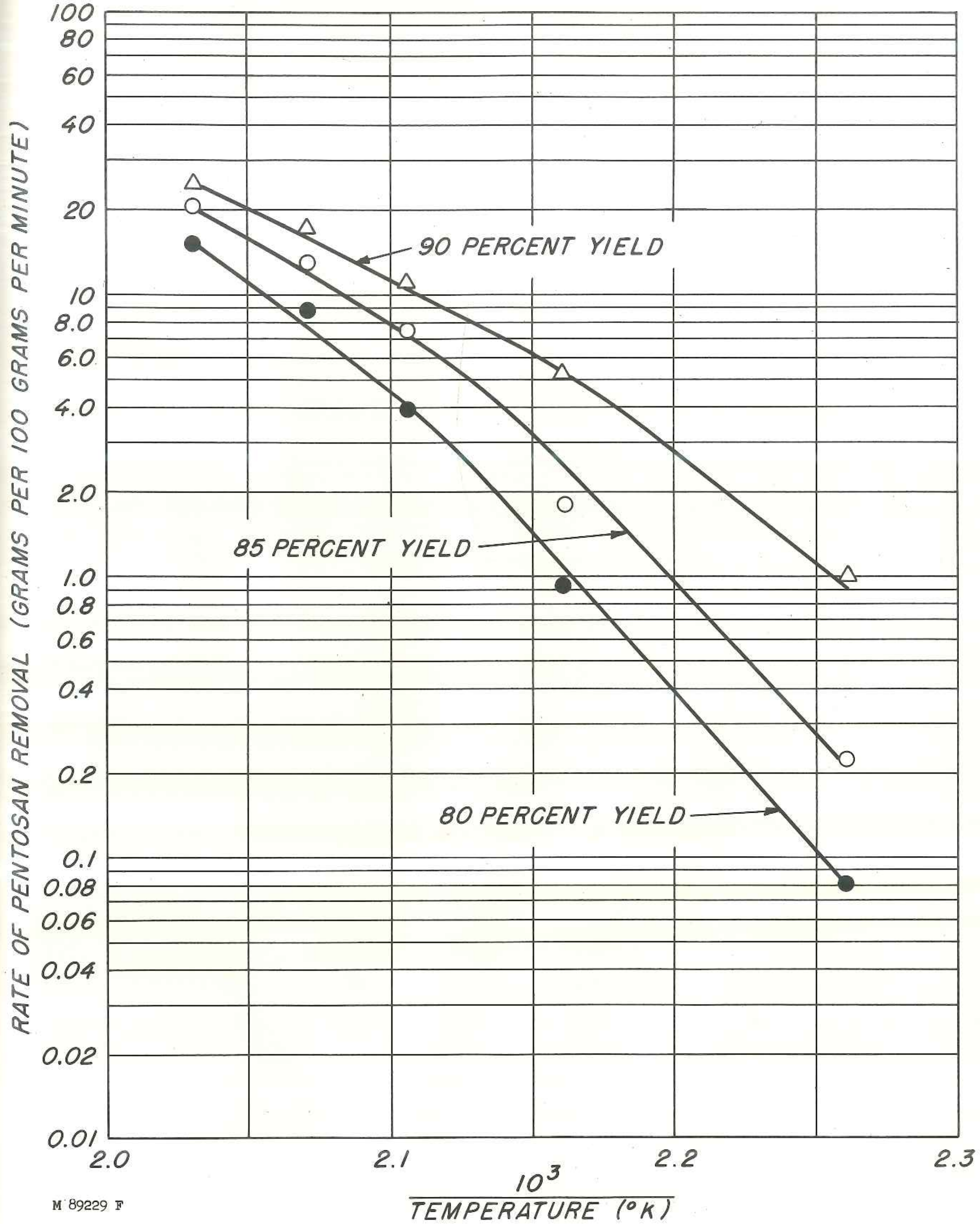


Figure 14.--Pentosan removal (percent of original pentosans present in wood) plotted against time for various liquor-wood ratios.



M 89238 F

Figure 15.--Rates of pentosan removal plotted against reciprocal absolute temperatures for various parameters of constant yield.



M 89229 F

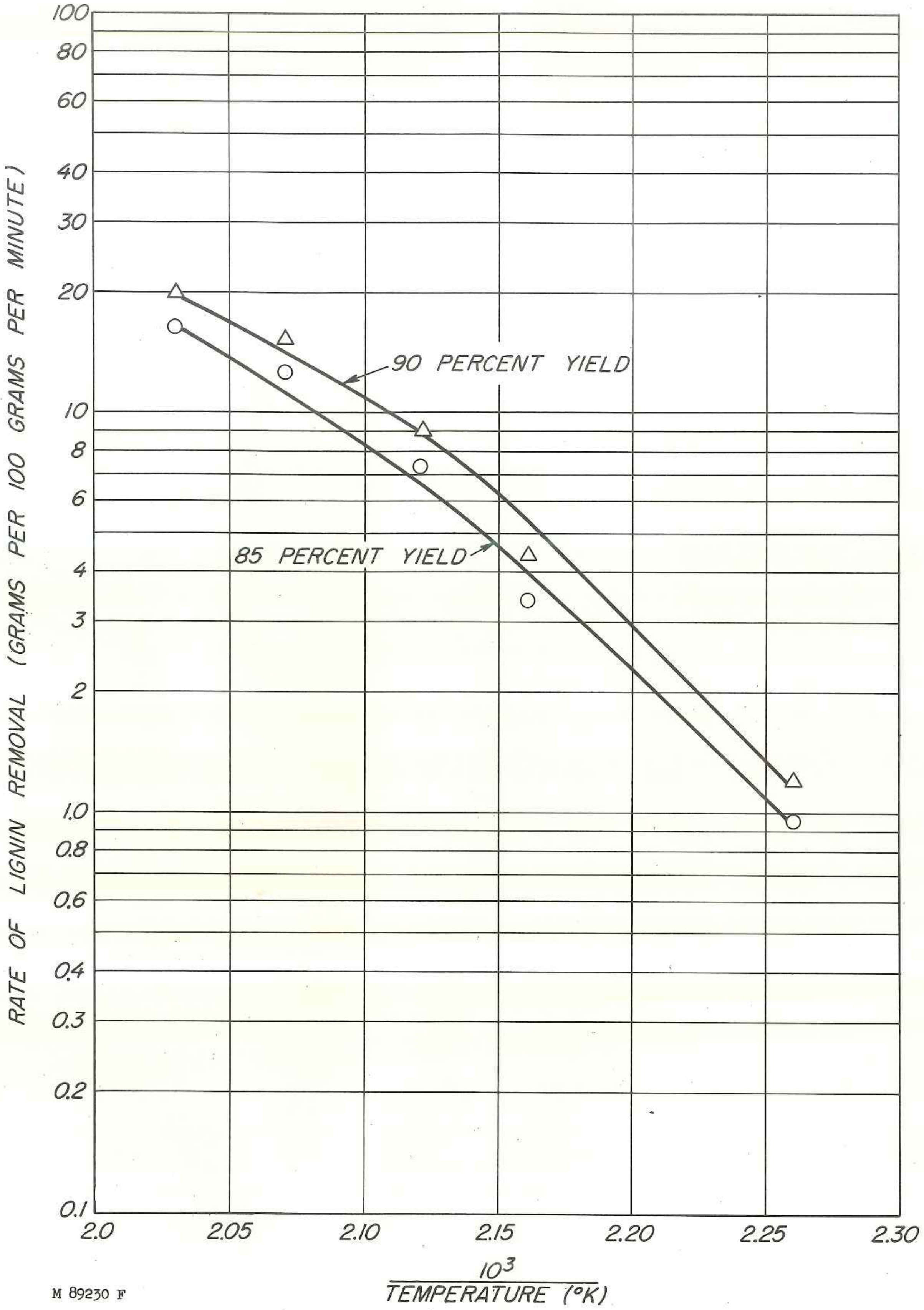
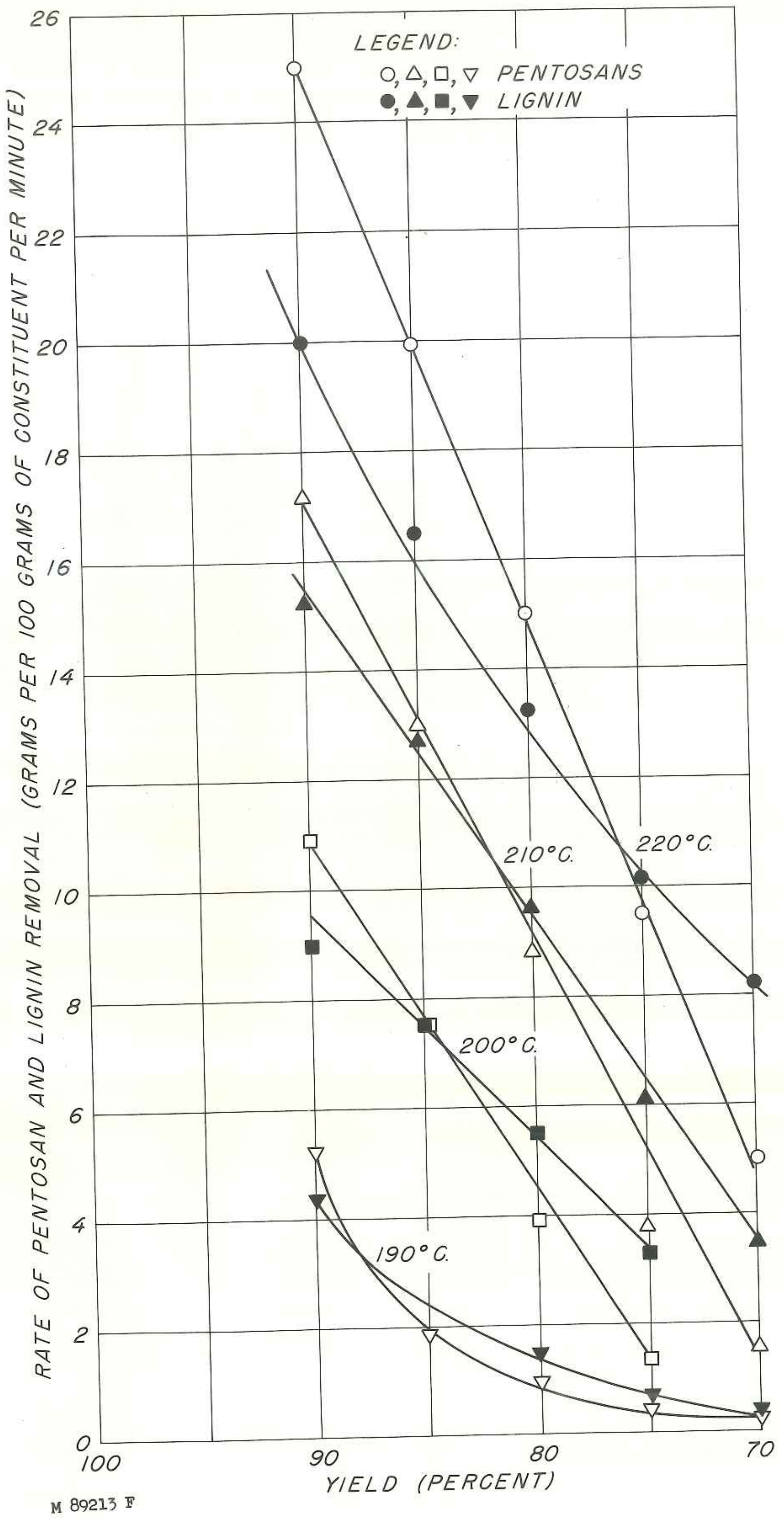


Figure 16.--Rates of lignin removal plotted against reciprocal absolute temperatures for various parameters of constant yield.

Figure 17.--Rates of pentosan and lignin removal plotted against pulp yields at various parameters of constant temperature.



M 89213 F

Figure 18.--Critical yields plotted against temperature.

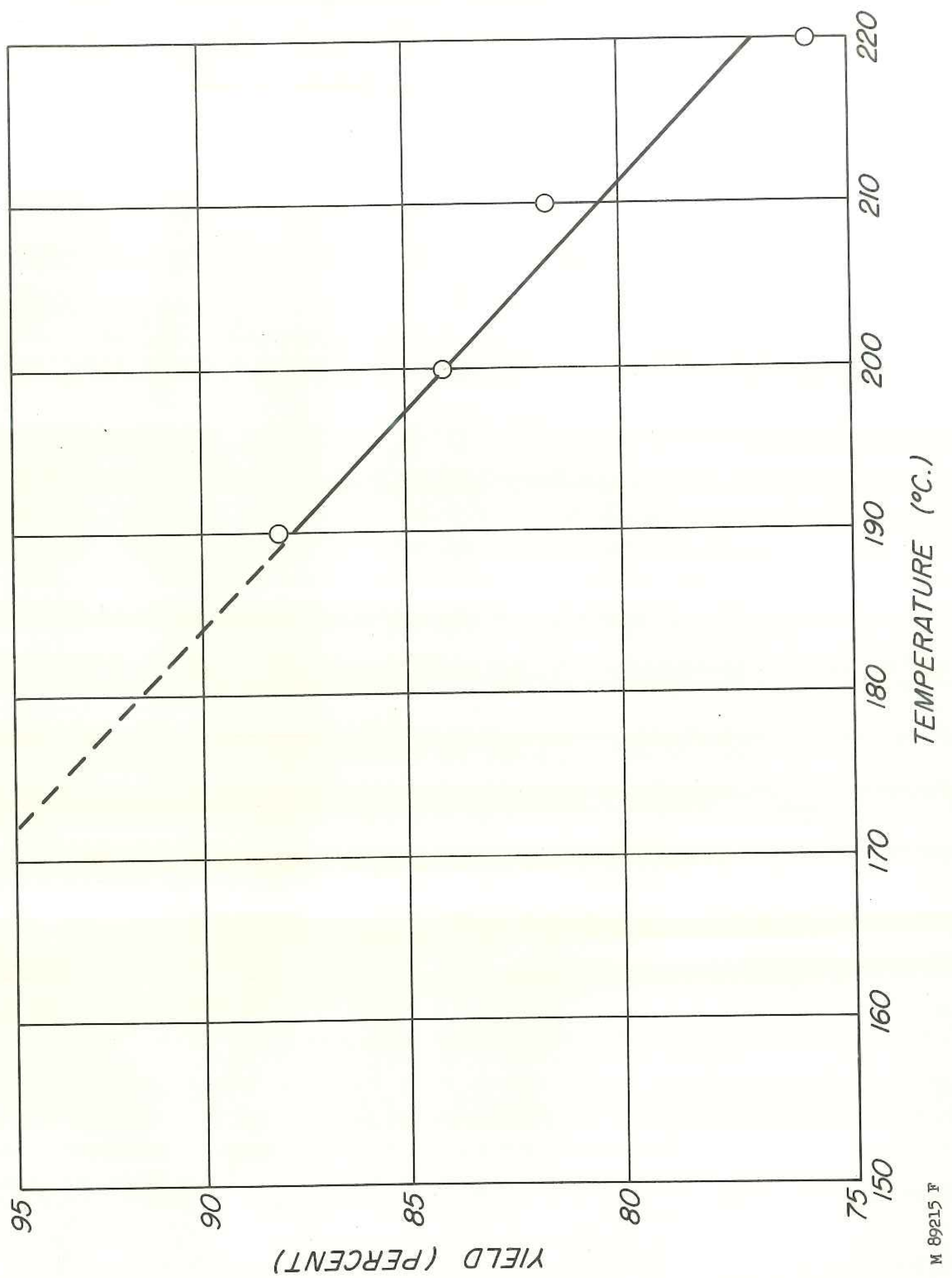
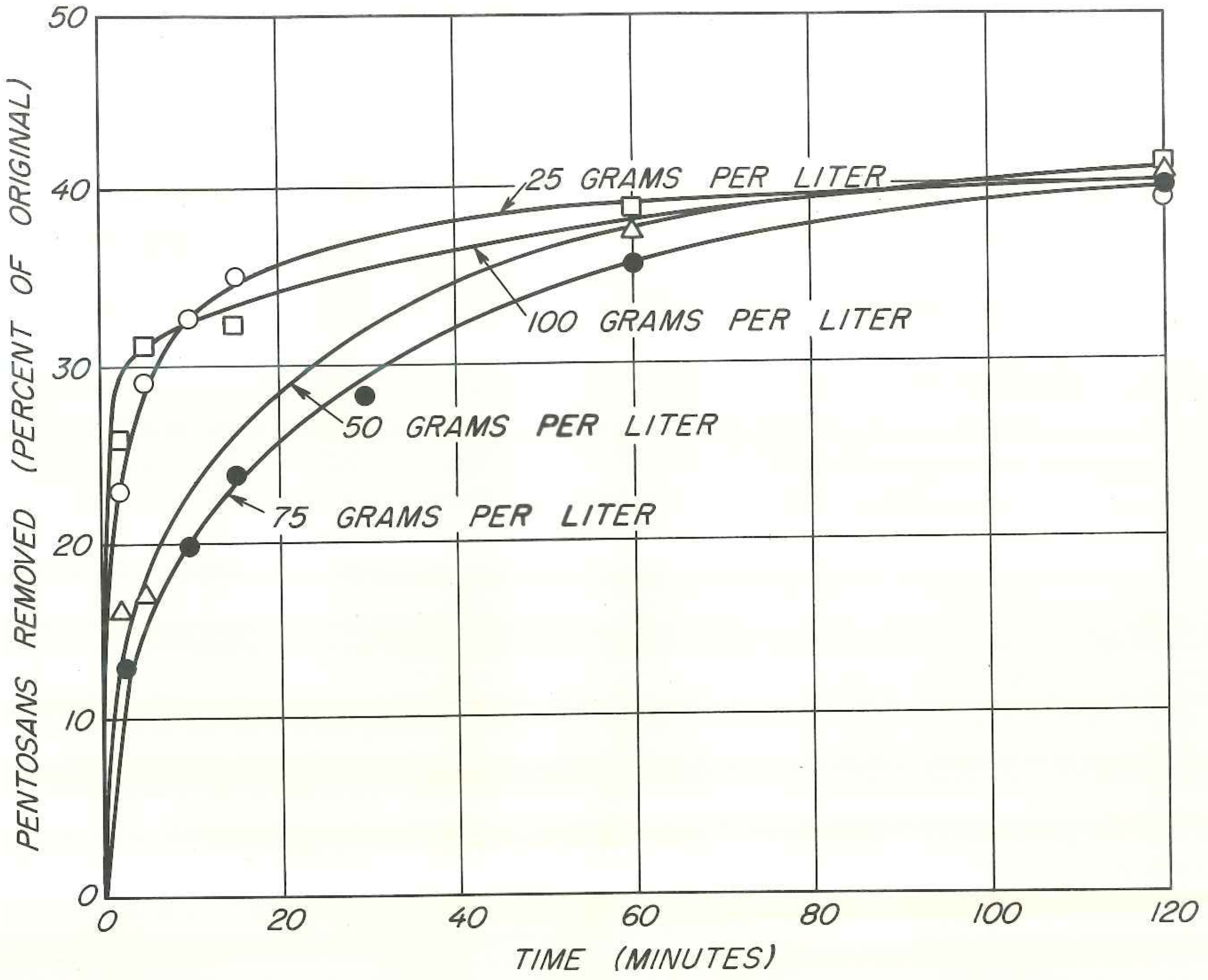
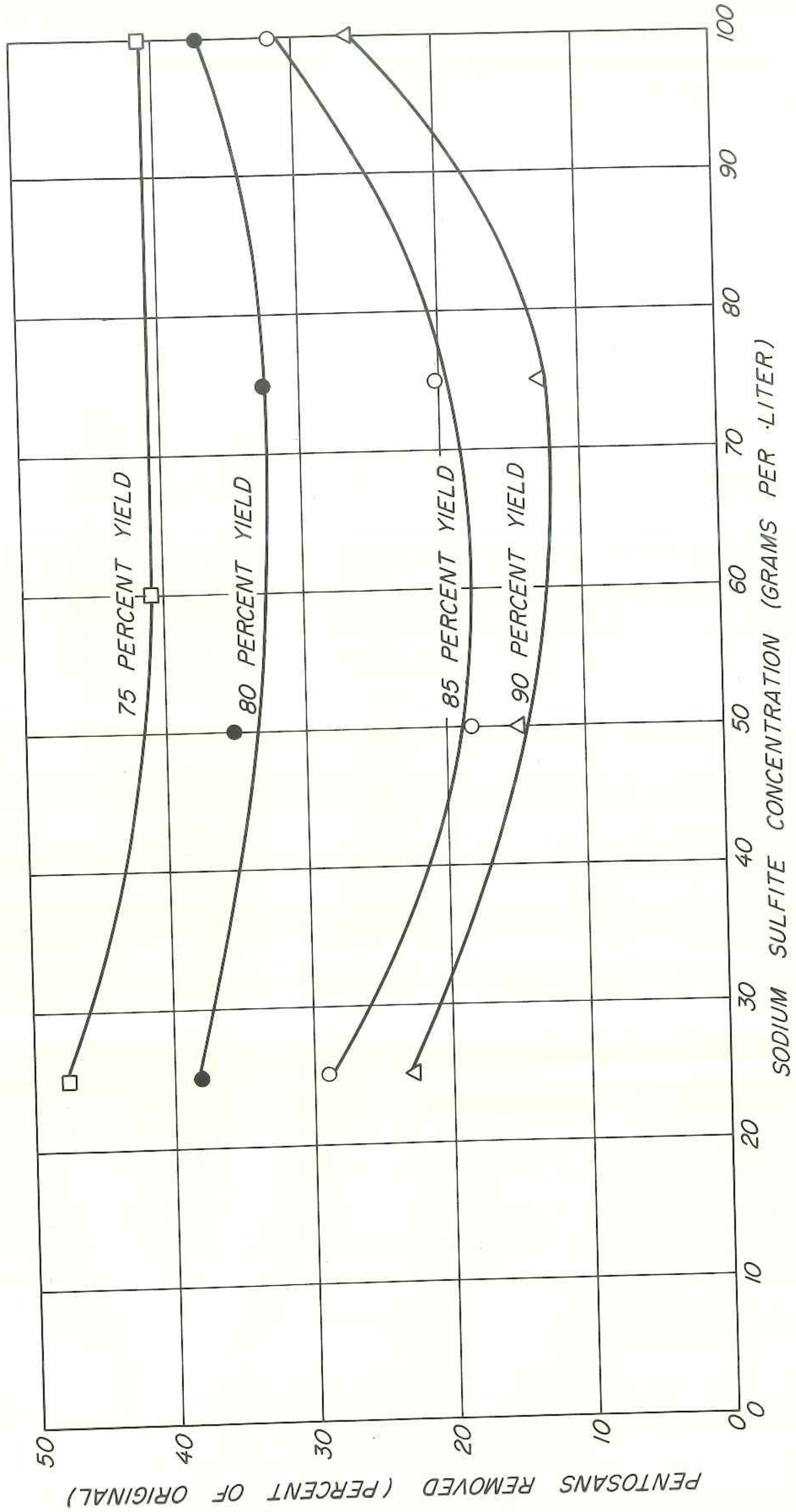


Figure 19.--Pentosan removal (percent of original pentosans present in wood) plotted against time for various parameters of constant sodium sulfite concentration at 170° C.



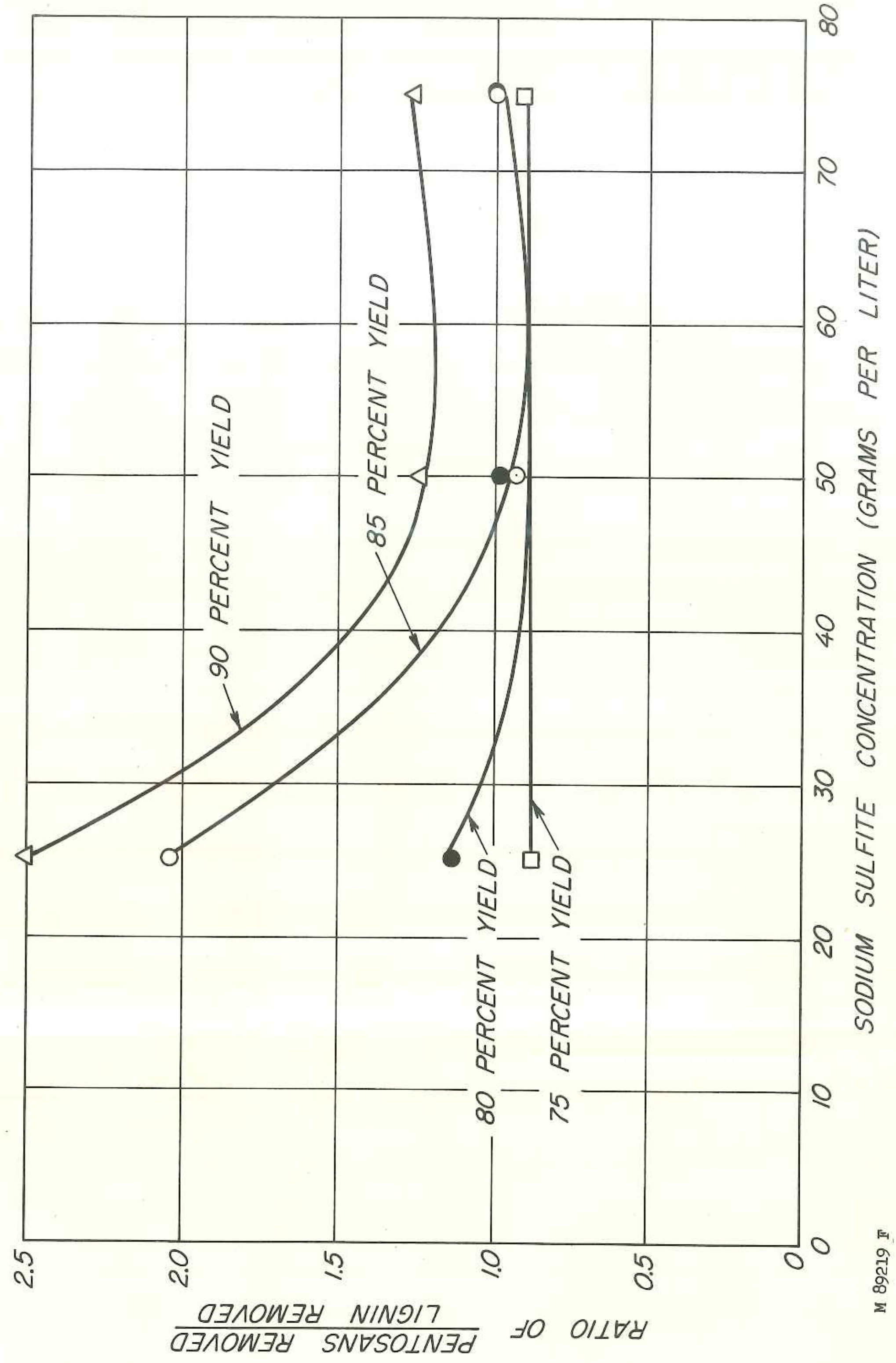
M 89212 F

Figure 20.--Pentosan removal plotted against sodium sulfite concentration for different parameters of constant yield at 170° C.



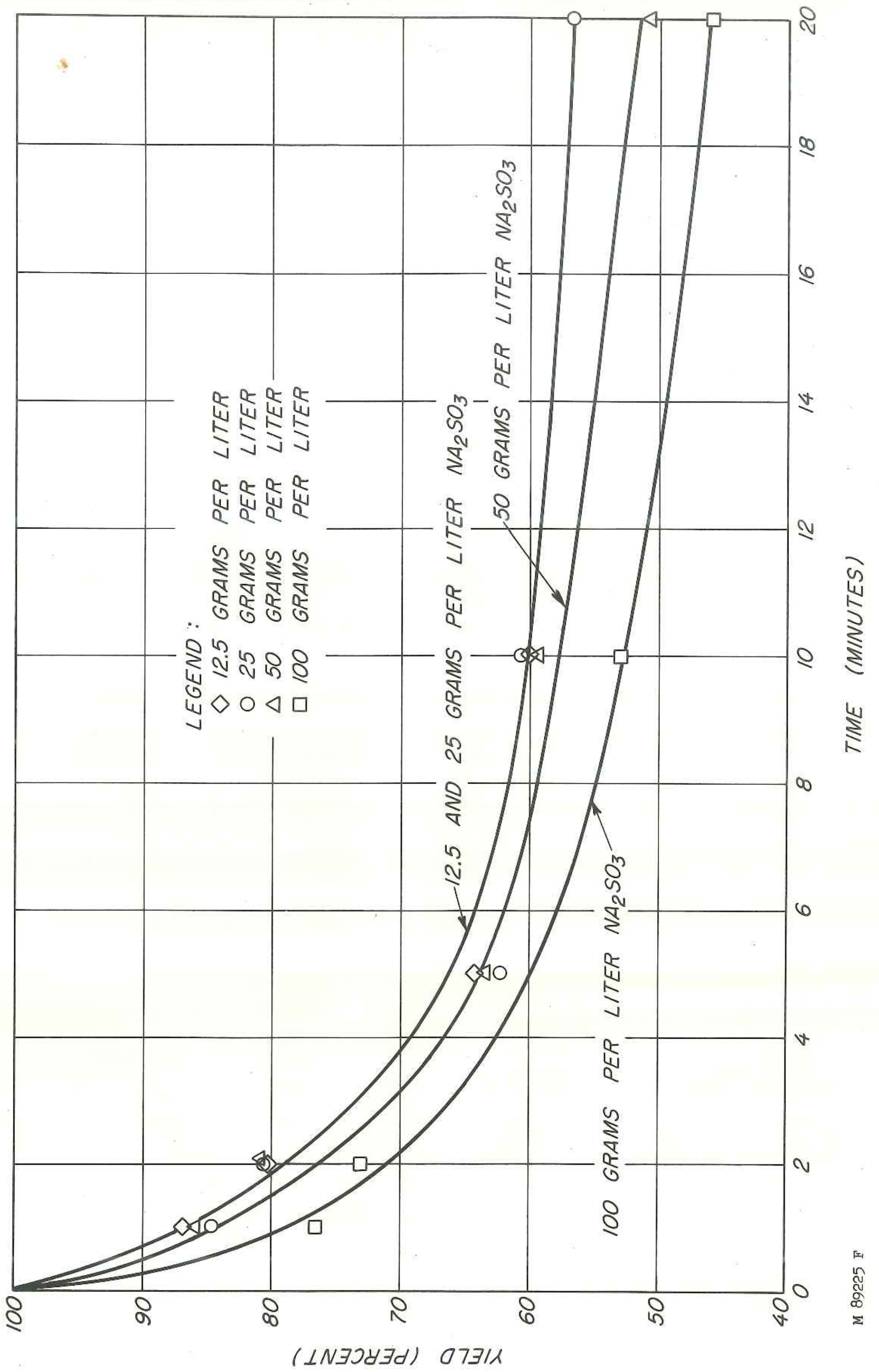
M 89211 F

Figure 21.--Ratio of pentosans removed to lignin removed plotted against sodium sulfite concentration for different parameters of constant yield at 170° C.



M 89219 F

Figure 22.--Total yields (percent of original oven-dried wood) plotted against time at different parameters of constant sodium sulfite concentration at 220° C.



M 89225 F

Figure 23.--Pentosan removal plotted against sodium sulfite concentration at various parameters of constant yield at 230° C.

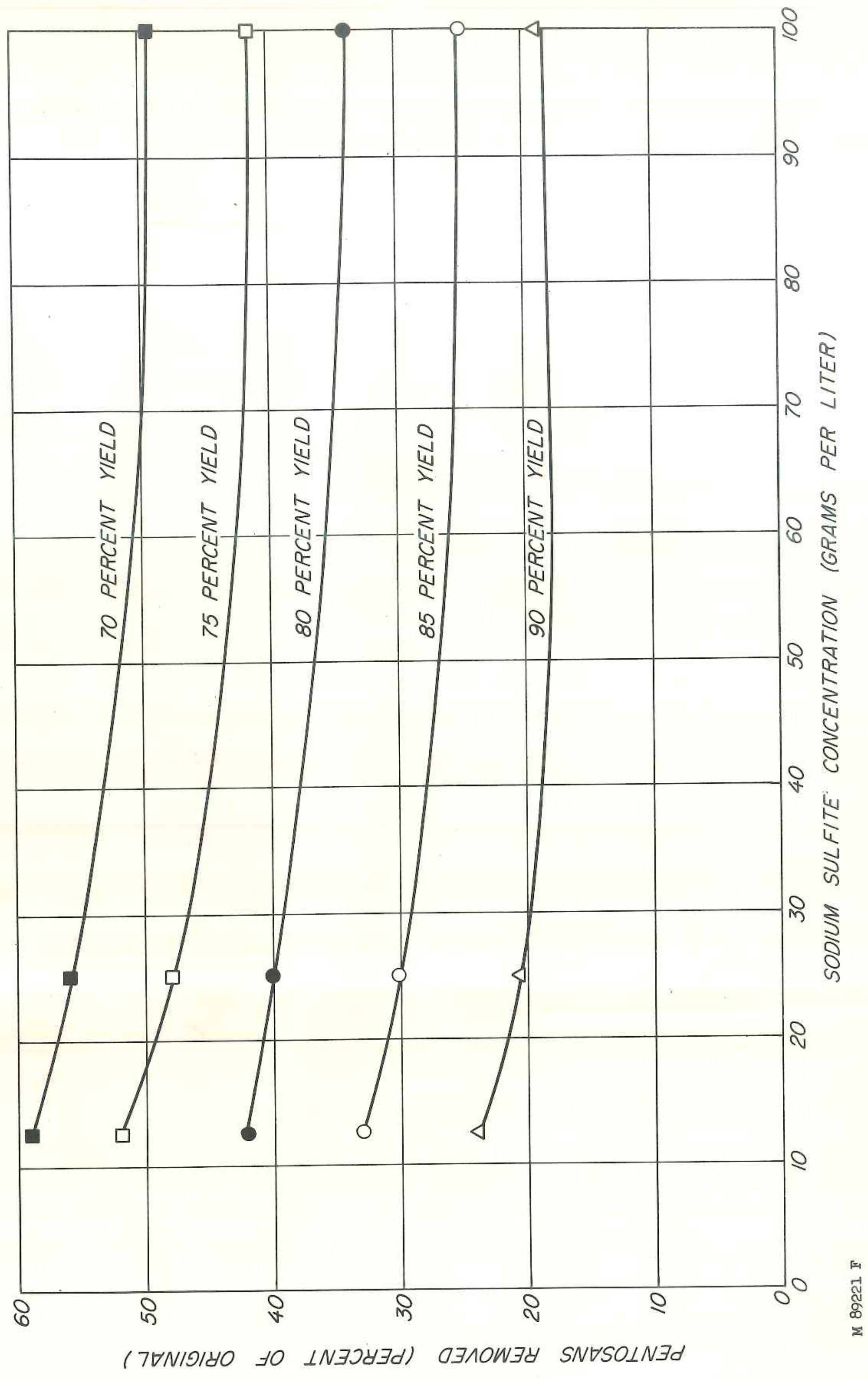
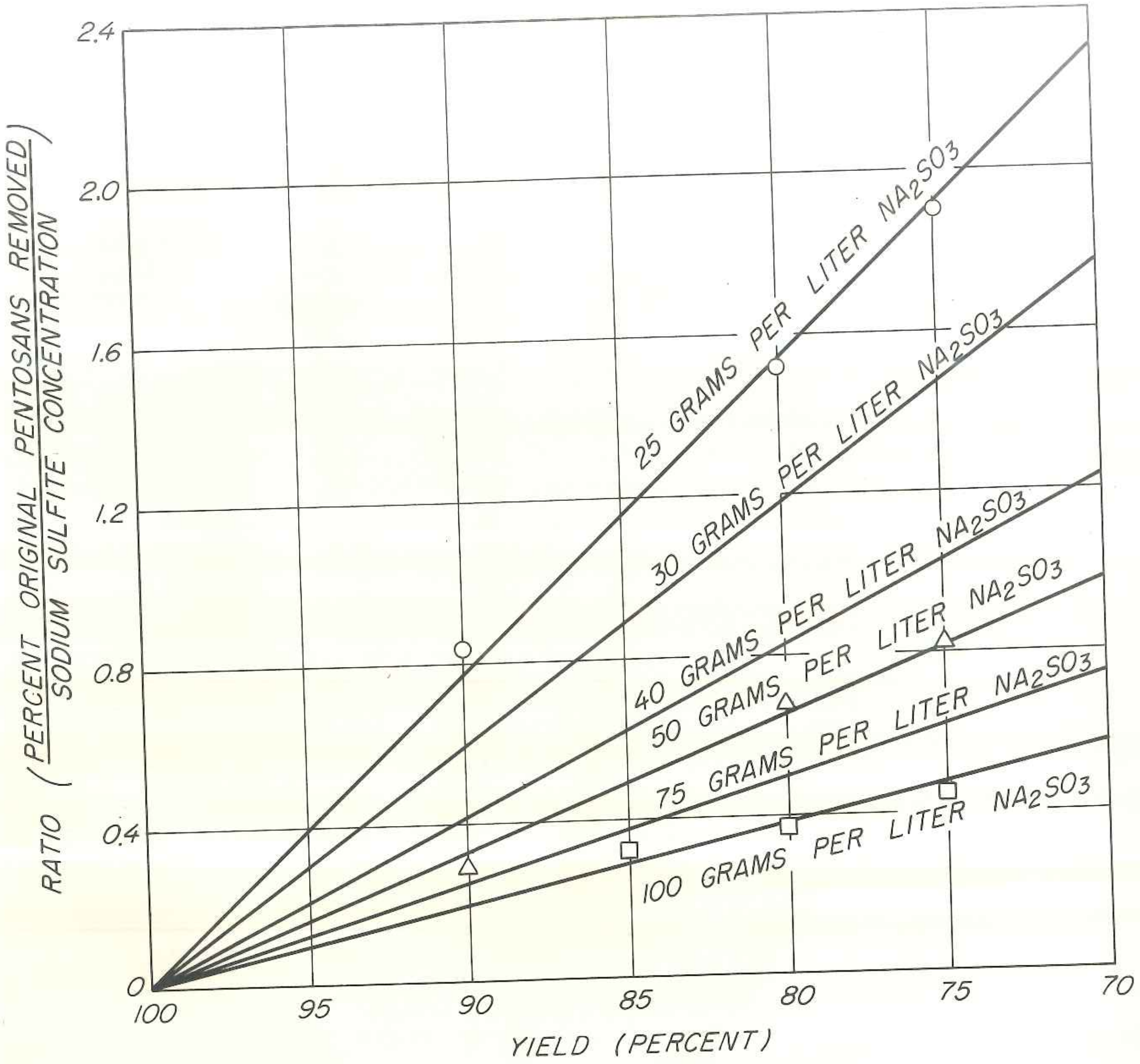


Figure 24.--Ratio of pentosans removed to sodium sulfite concentration plotted against total yield for various parameters of constant liquor concentration, at 170° C.



M 89235 F

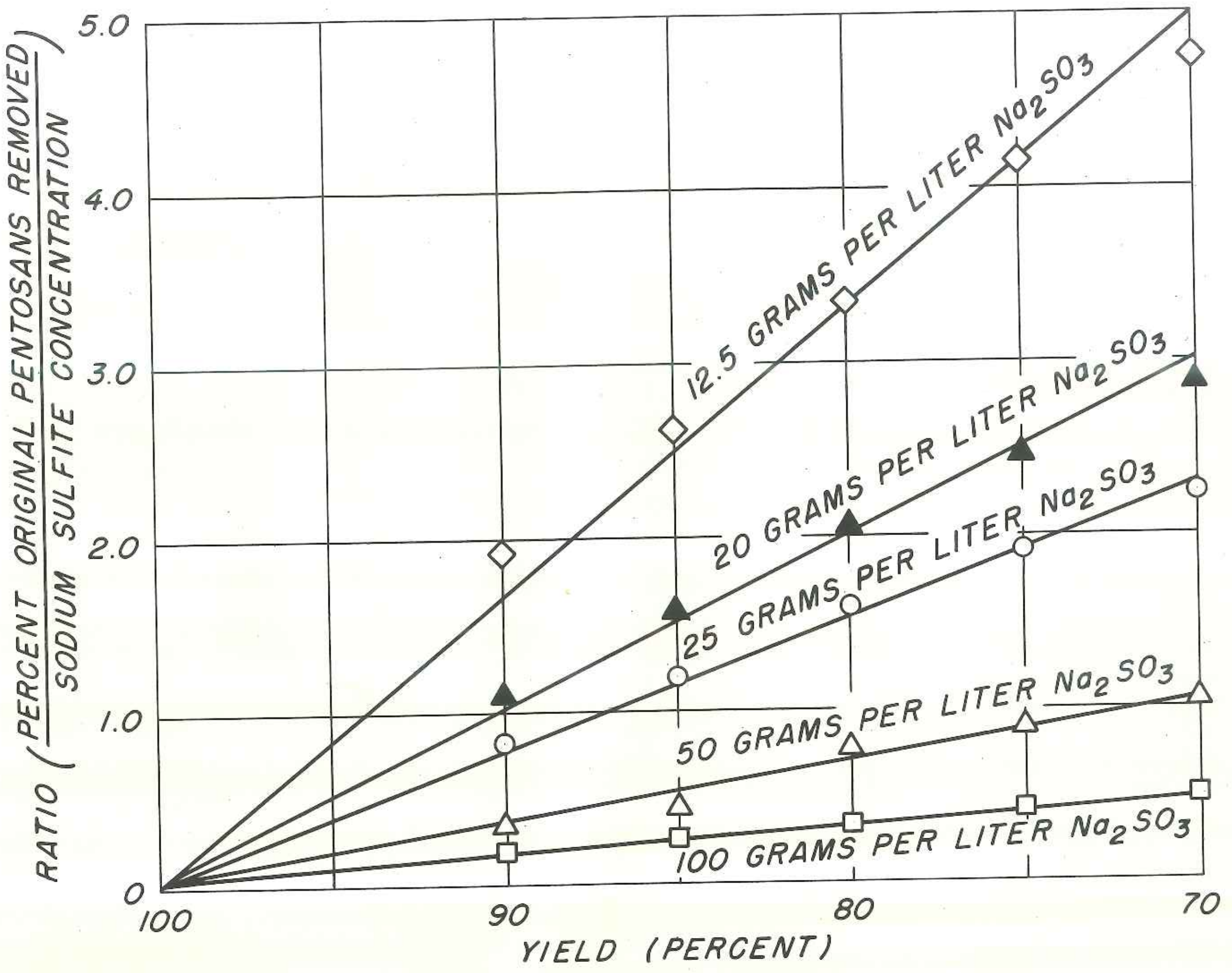
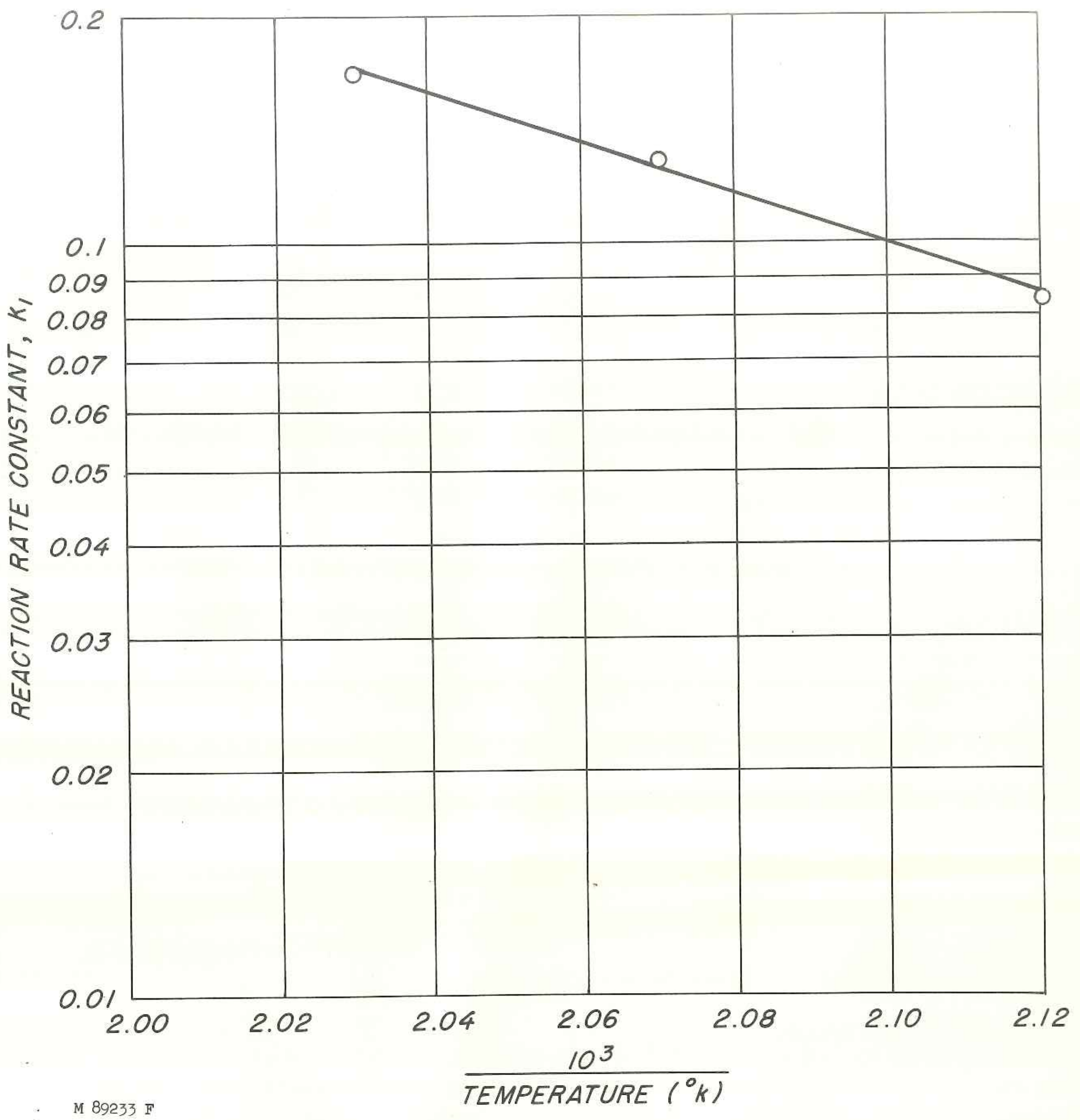


Figure 25.--Ratio of pentosans removed to sodium sulfite concentration plotted against total yield for various parameters of constant liquor concentration, at 220° C.

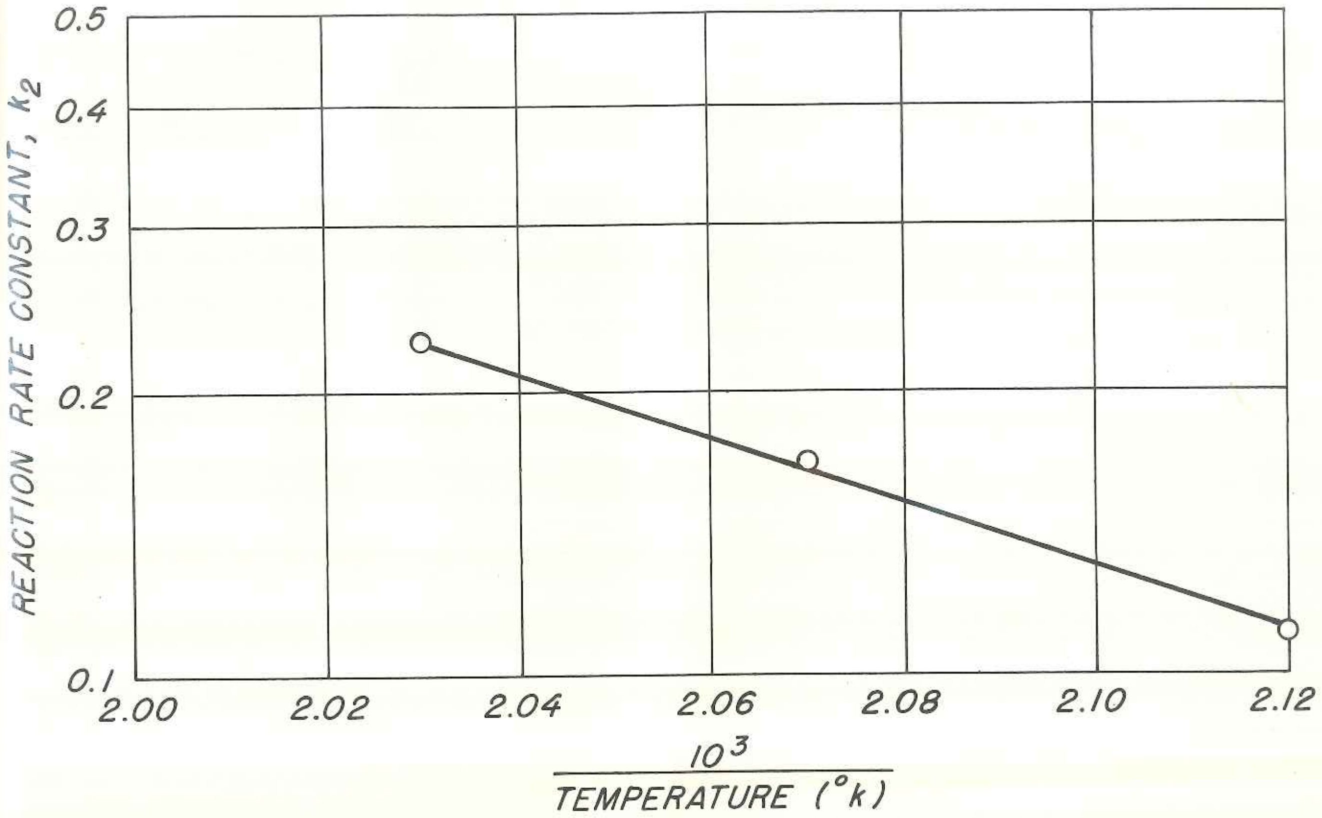
M 89231 F

Figure 26.--Reaction velocity constants, k_1, for lignin removal plotted against reciprocal absolute temperatures.



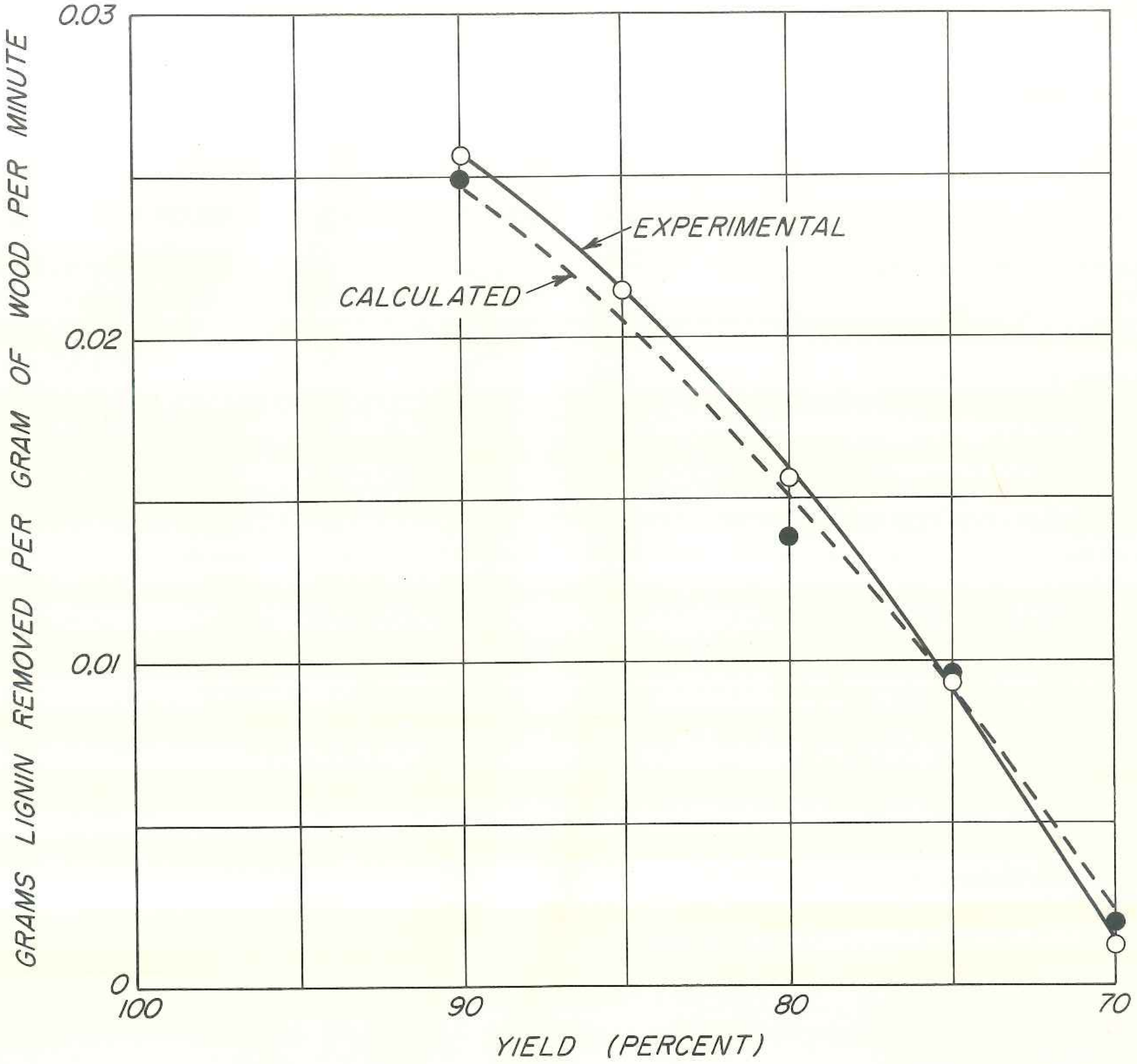
M 89233 F

Figure 27.--Reaction velocity constants, k_2, for total carbohydrate removal plotted against reciprocal absolute temperatures.



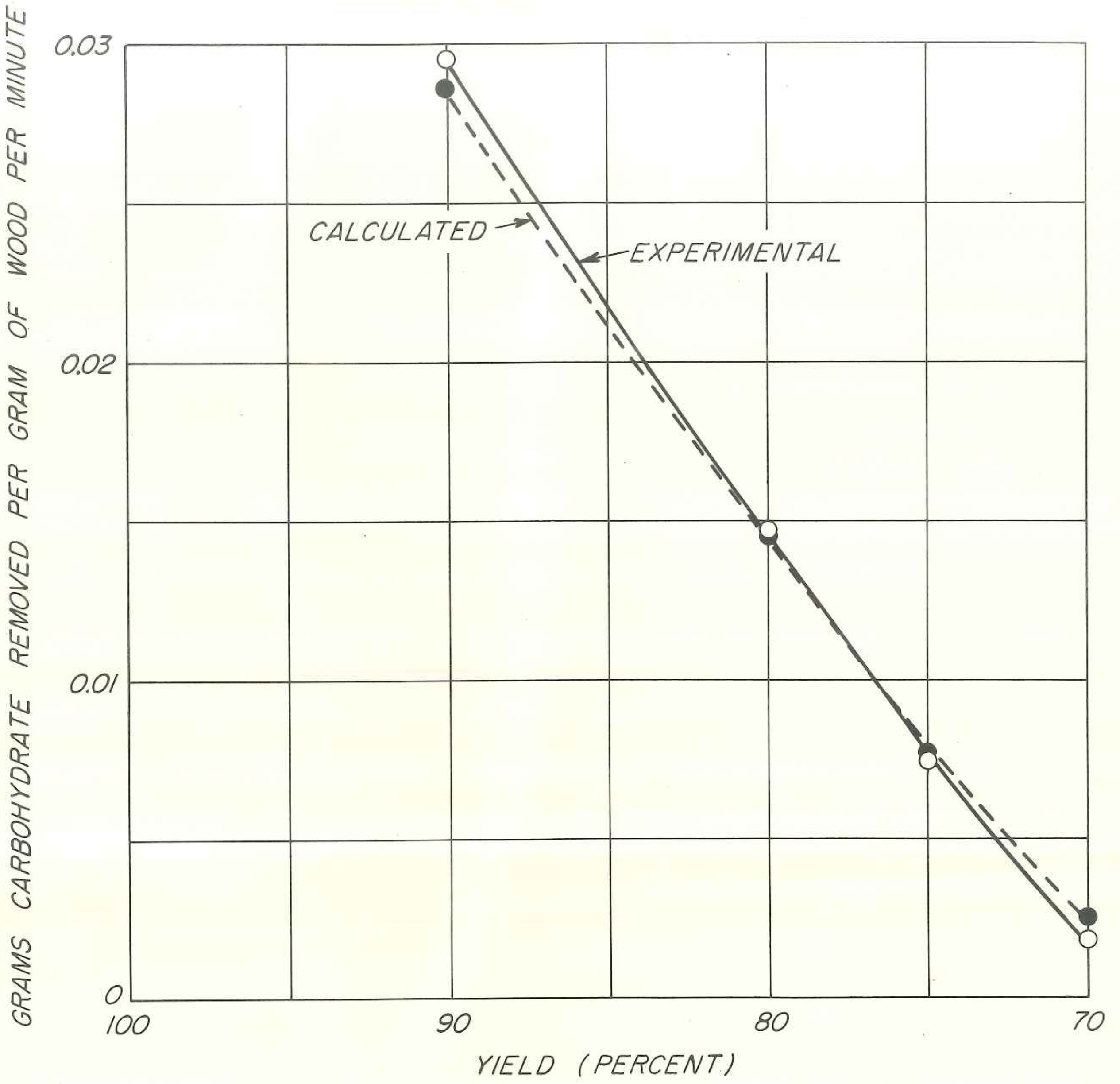
M 89237 F

Figure 28.--Calculated and experimental reaction rates for lignin removal plotted against pulp yield at 200° C.



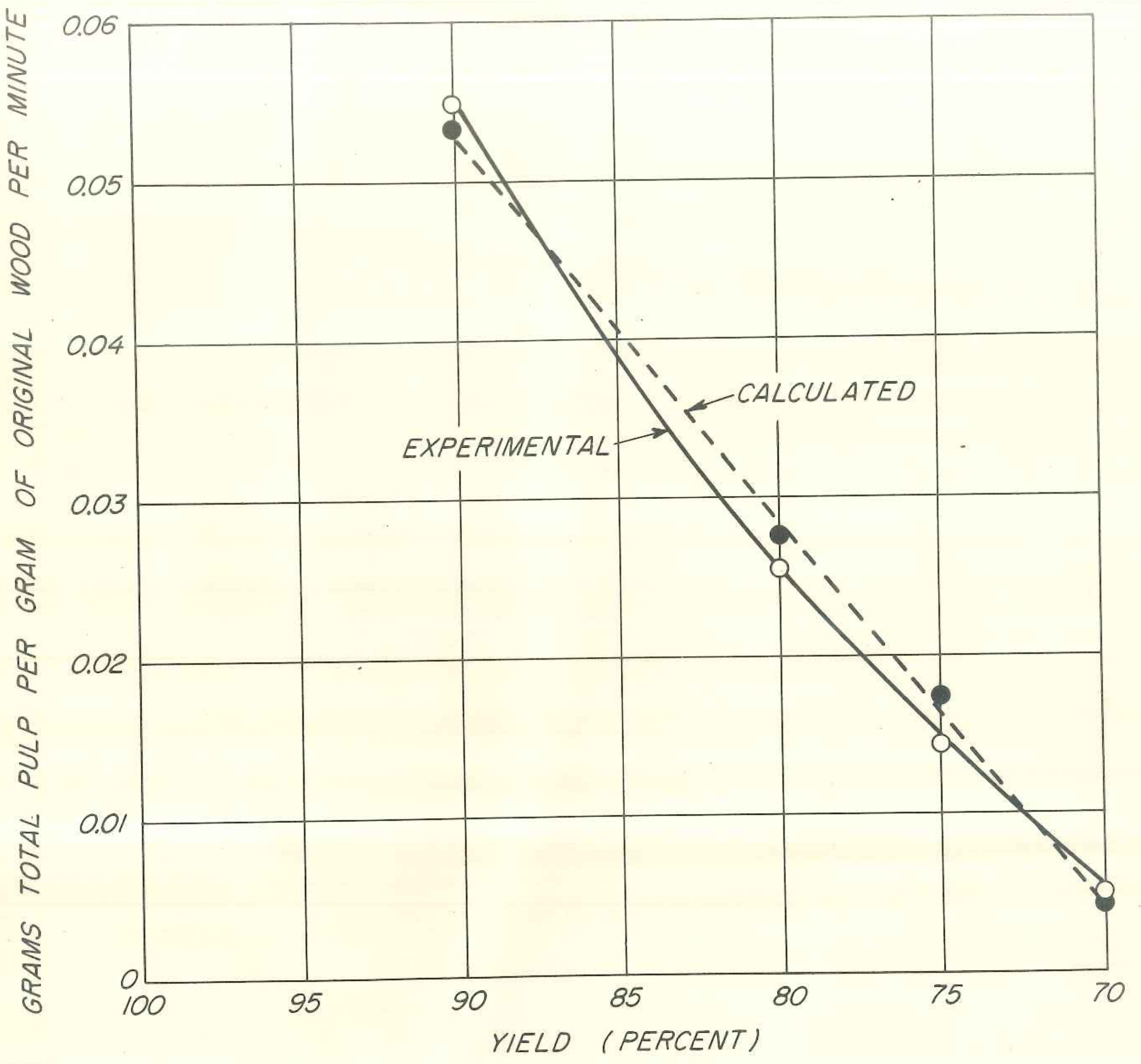
M 89236 F

Figure 29.--Calculated and experimental reaction rates for total carbohydrate removal plotted against pulp yield at 200° C.



M 89234 F

Figure 30.--Calculated and experimental reaction rates for total pulp yield plotted against pulp yield at 200° C.



M 89232 F