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The Effect of Elevated Temperatures
on the Neutral Sulfite Pulping Process

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THE EFFECT OF ELEVATED TEMPERATURES
ON THE NEUTRAL SULFITE PULPING PROCESS

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SUMMARY

The first step in determining the independent effect of pulping temperature on the chemical reactions involved in neutral sulfite pulping of aspenwood was the development of an isothermal digester. This digester was capable of heating or quenching the chip charge over a wide temperature range during a time lapse of only a few seconds. Hence, pulping with this equipment was approximately equivalent to cooking at isothermal conditions.

Five "Isothermal" cooks were made at each of four temperature intervals (173, 186, 200, and 210°C.). The pulping time of each cook was varied so as to space pulp yields over the range 45 to 75%. The pulps obtained were examined for both chemical and physical properties and the following temperature effects were observed when comparisons were made on the basis of equivalent yield.

1. Increasing pulping temperature greatly accelerated the chemical reaction rates normally associated with neutral sulfite pulping.
2. Over a 37°C. range in pulping temperature the increase in residual lignin amounted to about 1%.
3. Increasing pulping temperature decreased the average degree of polymerization, decreased the pentosan content and decreased the amount of alkali-soluble material remaining in the pulp, but did not affect the amount of alkali-resistant material.
4. Increasing pulping temperature increased the tear factor, decreased tensile strength, increased opacity, decreased brightness, and decreased stretch. However, the effects observed were small.
5. Chemical and physical evaluations both indicated that high-temperature pulps had a slightly lower intrinsic fiber strength, and a lower fiber-to-fiber bonding capacity at the same beating time than did low-temperature pulps.

INTRODUCTION

BACKGROUND OF THE PROBLEM

Neutral sulfite pulping has rapidly developed into one of the major commercial pulping processes, with particular success in those areas requiring high yield pulps. Pulping to low yields has been limited, in part, by the long digestion time required (1). Recently, there has been an increasing interest in reducing digestion time and applying continuous techniques to this pulping process.

Continuous operation differs from batch operation in that continuous digesters usually operate at a relatively constant cooking temperature. Extended periods of heating and quenching are virtually eliminated, and with them, the penetration period associated with batch digesters. In addition, continuous operation is usually more practical when used in conjunction with short reaction times (2). Hence, it has become increasingly important to understand the effects involved in the neutral sulfite pulping reaction, especially at elevated temperatures.

Much information indicating the influence of pulping variables on the neutral sulfite process has been reported, based on pulping experiments conducted under batch conditions. Under such conditions, concentration, pH, and temperature all vary over a substantial portion of the cook, and a clear understanding of the independent effect of each of these variables has not been obtained.

LITERATURE SURVEY

Commercially, neutral sulfite cooks have generally been conducted at maximum temperatures of about 170°C. At this temperature level, the over-all cooking time varies from a few minutes to a few hours, depending upon the final yield desired and the exact cooking schedule employed. For yields below approximately 60%, digestion time is greatly extended.

Studies conducted on batch operations indicate that in the temperature range of 140-180°C., the neutral sulfite pulping reaction behaves similarly to many organic chemical reactions, in that the pulping rate a little more than doubles for each 10°C. increase in reaction temperature (3, 4, 5, 6). Thus, one could conclude that shorter cooking times could be obtained by the use of higher pulping temperatures. However, the pulping reaction is not a single chemical reaction, but rather a series of reactions, whereby both lignin and carbohydrate materials are removed. Several investigators (3, 7, 8, 9) state that at very high temperatures (above 170°C.), pulps of the same yield have less carbohydrate and this is more degraded. If this is true, the use of accelerated reaction by increasing temperature might be undesirable.

However, this conclusion on the effect of elevated temperature is open to some question. The data giving rise to this conclusion were usually based on comparisons of pulps produced at different cooking temperatures but not at equivalent yields. Frequently, the period of heating and quenching was ignored or omitted in the determination of over-all reaction time. If it is assumed that the pulping reaction rate doubles with each 10°C. increase in reaction temperature, four hours at

170°C. are equivalent to only seven and one-half minutes at 220°C. Most batch laboratory digesters require more than thirty minutes to reach temperatures of 180°C.; hence, overcooking could occur even before maximum operating temperatures were reached.

Not all of the previous experimental data indicate that elevated pulping temperatures cause excessive cellulosic degradation. In the temperature range of 140-180°C., Bray and Eastwood (4) showed that the relative rates of removal of lignin, pentosans, and cellulose do not materially change with change of digestion temperature. Similar conclusions were derived by many other investigators (5, 8, 10, 11, 12, 13, 14, 45), and it appears unlikely that the effect of temperature should undergo a marked change with additional increase. The importance of cooking time when pulping at elevated temperatures cannot be overemphasized. In the Masonite process, where temperatures are in the range of 250-285°C. (15), the time-temperature relationship is so important that as little as one-half second difference in cooking time will greatly alter the fiber being produced (16, 17). Cellulose itself can be converted to a black carbonaceous mass at temperatures of 290°C. (10), and gelatinization will occur at temperatures of about 215°C. (18). But, by limiting the time at maximum temperature, usable fibers have been produced at temperatures as high as 280°C. (15, 18, 19).

In a survey of the literature only one study at elevated temperatures was found where careful consideration was given to the time-temperature relationship. Doraiswamy (5) studied the neutral sulfite process at

temperatures as high as 220°C. He pulped aspenwood meal with a solution of sodium sulfite in such a manner that digestion heat-up and quenching time was limited to less than five minutes. The pulps obtained were examined for total carbohydrate, pentosans, and lignin by difference. (A portion of Doraiswamy's data can be found in Table I.) His data showed that increasing pulping temperature greatly accelerated the overall pulping reaction rate. The data at 90 and 80% indicate preferential removal of carbohydrate whereas at 70% yield there may be preferential removal of lignin at higher temperatures. Thus, many questions with respect to the changes in the chemical pulping reactions at elevated temperatures still remain unanswered.

TABLE I

DORAISWAMY YIELD DATA

Temp., °C.	90%		80%		70%	
	Yield, cooking time, min.	Pulps, % lignin removed	Yield, cooking time, min.	Pulps, % lignin removed	Yield, cooking time min.	Pulps, % lignin removed
170	7	23	60	38	—	—
190	2	18	10	36	60	44
200	1.5	15	4	38	20	57
210	0.6	13	2.1	30	8	62
220	0.4	10	1.5	20	4	53

Per cent lignin removed expressed in percentage, based on the original lignin content of the wood.

STATEMENT OF THE PROBLEM

The objective of this study was to determine the effect of pulping temperature in the range 170-210°C. on the chemical and papermaking properties of pulps produced by the neutral sulfite pulping of aspenwood. To accomplish this it was necessary to develop equipment which would essentially eliminate the heating and quenching period normally associated with pulping.

THE EXPERIMENTAL PROGRAM

EXPERIMENTAL CONSIDERATIONS

In this thesis, the factors associated with impregnation were minimized.

The time required for impregnation can be reduced by subdividing the wood mechanically prior to pulping, and thereby providing greater surface areas and shorter distances over which impregnation must occur. An objection to such treatment is that the physical strength characteristics of pulp produced from subdivided wood may suffer because of mechanical damage to the fibers. However, McGovern and Simmonds (20) showed that chips could be reduced in cross-sectional area without any significant effect on the chemical or physical properties of pulps produced from these chips. Thus, it was concluded that some form of mechanical subdivision which would affect only the cross-sectional area, but would not damage the length of the fibers, would be suitable for the experimental conditions in this thesis. Furthermore, since all the pulps would be produced in a standard manner, the relative effect of temperature probably could be determined, even though the maximum obtainable pulp strength might not be achieved. After consideration of several methods of subdividing, veneering was chosen. This provided an extremely uniform physical state for the raw material.

Further reductions in impregnation time were accomplished by limiting the investigation to the pulping of aspen sapwood. Experiments

(21) have shown that aspen sapwood is impregnated much more rapidly than heartwood, especially if it is subjected to a vacuum just prior to flooding with cooking liquor (22). Laboratory experiments on the flooding of sapwood veneer were conducted. Sapwood veneer of the type used in this thesis¹ was subjected to a vacuum and then flooded with water. Water impregnation into the wood structure was sufficiently rapid under these conditions to cause the wood to lose its buoyancy in less than one second. Hence, it was concluded that the use of sapwood veneer in conjunction with a vacuum would reduce liquor impregnation time to about one second. This short impregnation time should remain approximately constant from cook to cook, and hence can be added to the time required for chemical reaction without introducing any appreciable error in the conclusions that might be derived.

Another factor, closely related to impregnation, which can also influence chemical reaction rates is that of diffusion during pulping. If insufficient chemical penetrates into the wood initially, then inorganic reagent must diffuse into the chip from the bulk solution during pulping. This rate of diffusion is greatly affected by many variables, such as circulation within the digester. In order to minimize this factor, a cooking liquor of high concentration was used. Thus, after impregnation, it was estimated that the wood contained within itself sufficient inorganic reagent for complete reaction.

Commercially, neutral sulfite cooking liquor consists of a solution of sodium sulfite buffered with sodium bicarbonate, but it is not unusual

¹ See page 26.

to find other buffers being used. Sodium sulfite, itself, if present in sufficient amount, will act as a buffer. It has been shown experimentally that the pulping reaction and chemical composition of resulting pulps vary only slightly with kind and extent of buffering reagent (23). Hence, in this thesis, the cooking liquor consisted of pure sodium sulfite in sufficient amount for buffering and chemical reaction (110 g./l.).

ISOTHERMAL DIGESTER DESIGN

To obtain data which would successfully isolate and reveal the effect of pulping temperature per se, it was desirable to pulp at conditions approaching isothermal operation. This meant that the heating and quenching of the cooking mass had to be accomplished almost instantaneously. Furthermore, the equipment used for cooking must be capable of withstanding the vapor pressures associated with increased pulping temperatures. To meet these specific requirements, it was necessary to design and construct a digester, henceforth referred to as the "isothermal digester".

The capacity of the isothermal digester was determined from experimental requirements. It was desirable to produce sufficient pulp in a single cook to provide material for a complete chemical and physical evaluation. The minimum sample size was calculated and was found to be about 800 grams on the oven-dry wood basis (40% yield was considered to be the lowest yield of interest). The packing factor of wood veneer of the size used in this thesis was measured, and the minimum digester volume was found to be about 12 liters.

The packing factor of the wood veneer also dictated the minimum liquor-to-wood ratio (13 to 1) that would provide complete chip coverage. The digester size and the very high liquor-to-wood ratio made it obvious that large quantities of heat were going to be involved in heating or quenching the digester. It was felt that conventional use of heat exchangers would not handle the amounts of heat involved, in the time available, and with the required degree of control. Hence, it was necessary to find some other means of heating and quenching the isothermal digester.

Most of the energy involved in heating is used to create a temperature change in the metal of the digester and in the cooking liquor. Thus, a very rapid temperature change with a small energy exchange could be accomplished on the wood itself by separate preheating of the liquor and digester. The heating of the isothermal digester was accomplished by this approach, using various techniques of separate preheating, followed by a rapid heat exchange to the wood itself. Quenching was accomplished by reversing the procedure, that is, separating the components and then cooling.

Two separate pressure vessels formed the basis of the isothermal digester. The cooking liquor was heated to an appropriate temperature in one vessel while the wood was contained in the second. The vessel containing the wood was provided with electrical heaters so that its shell wall could be preheated to any desired temperature. However, suitable precautions (which will be described later) had to be taken in this vessel

to prevent heat transfer from the hot vessel walls to the wood charge. If the temperature of the wood should increase appreciably with the wood not in intimate contact with cooking liquor, degradation could occur. Such degradation would alter the chemical and physical characteristics of the fibers and hence confuse or mask the effects of temperature during pulping.

A schematic drawing showing the design of the isothermal digester can be found in Figure 1. (More complete drawings are available from The Institute of Paper Chemistry.) This equipment has the following operational features:

1. Two pressure vessels, numbered 1 and 2, were attached to one another by suitable piping. Vessel No. 1, the larger of the two, was for preheating the cooking liquor to temperature; while Vessel No. 2 was that in which the actual pulping was accomplished.
2. An appropriate liquor charge was introduced into Vessel No. 1, where it was heated to the desired temperature by means of electrical heaters.
3. Wood veneer was packed into a specially designed stainless steel basket (described in the Appendix, page 111), and this basket was inserted into Vessel No. 2. After sealing, a vacuum (0.5 to 1.0 centimeters of mercury total pressure) was applied to the vessel. This vacuum prevented heat transfer by convection from the vessel wall to the basket and its contents, and also had the desirable effect of removing the major portion of air entrapped within the cell walls of the wood.¹ The basket was specifically designed to act as a radiation shield, thereby minimizing heat transfer to the wood by radiation. Metal-to-metal contact between the basket and the vessel wall was avoided, reducing heat transfer by conduction to a negligible amount.
4. After the liquor was preheated, the basket properly positioned, and the shell wall of Vessel No. 2 was heated to the proper temperature, the cooking reaction was started by opening the

¹ See page 8.

FLOW DIAGRAM OF ISOTHERMAL DIGESTER

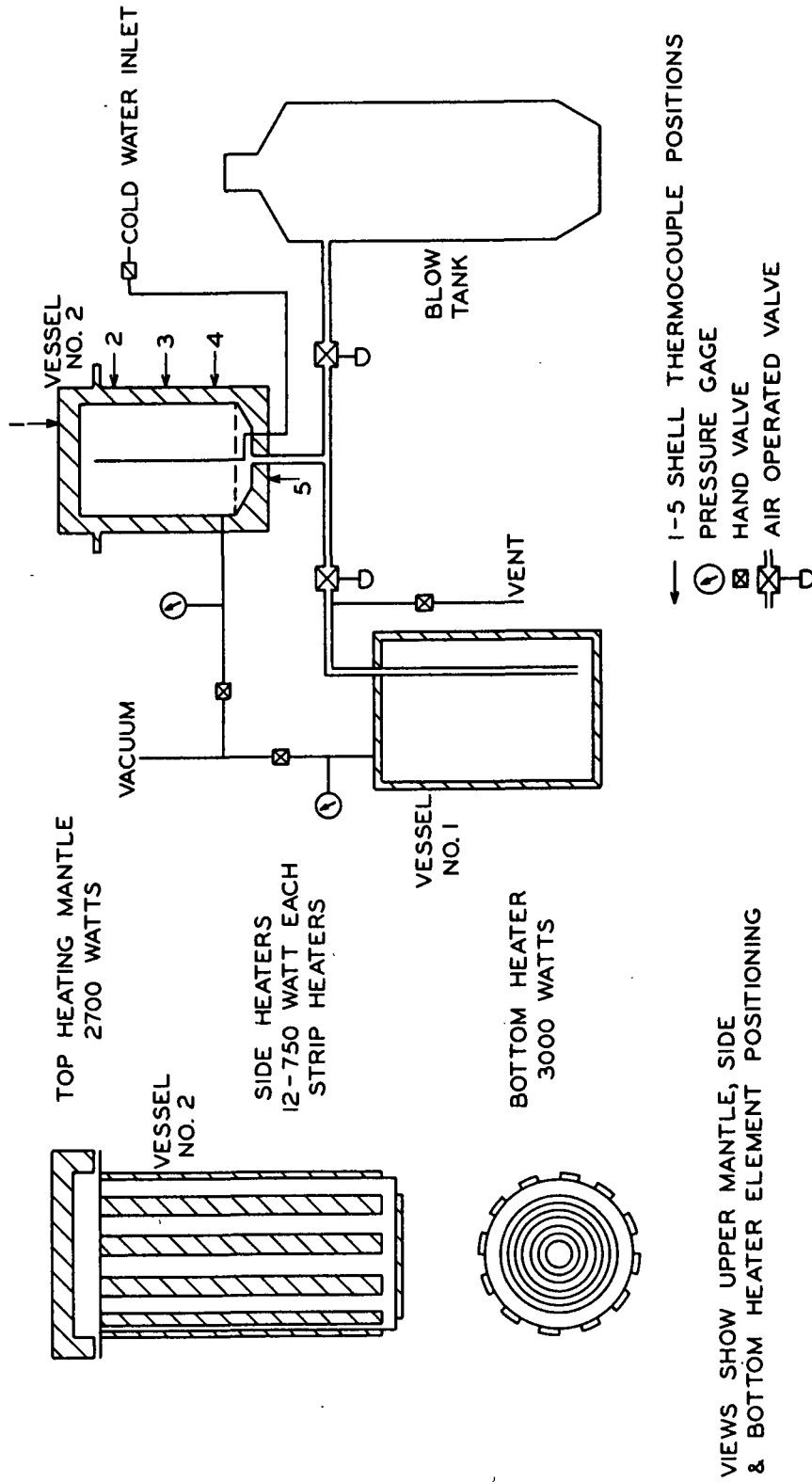


Figure 1. Isothermal Digester Design

line connecting the two vessels. This allowed the hot liquor to transfer from Vessel No. 1 to Vessel No. 2. By proper manipulation of conditions in Vessels 1 and 2, a very rapid temperature change was brought about within the wood itself.

5. Upon completion of cooking, the liquor content of the entire system was dumped by opening the relatively large line leading to the cyclone blowpit. As pressure dropped, cold water was injected into the center of the pulp mass, until such time as Vessel No. 2 could be opened and its contents removed.

Figure 2 is a picture of the pressure vessel (Vessel No. 1) used as a liquor preheater in the isothermal digester. As can be seen in this picture, the contents of the vessel were mechanically stirred and the power input to the electrical heaters was controlled by a rheostat. Both of these factors aided in the control of liquor temperature. Thermocouple measurements indicated that liquor temperature could be adjusted to within 0.2°C .

Figure 3 is a picture showing the cyclone blowpit and the pressure vessel (Vessel No. 2) in which the actual pulping occurred. It is also possible to observe in this figure the air-operated valve controlling the blow line. A similar valve was used to control the liquor transfer from Vessel No. 1 to Vessel No. 2. The use of such air-operated valves made possible a very rapid and positive opening or closing of appropriate lines.

Temperature was measured in the isothermal digester through the use of a network of iron-constantan thermocouples. Thermocouple potential was determined by either of two instruments (Cambridge Portable Potentiometer; Minneapolis Honeywell Brown Electronik Recorder, Type 153),

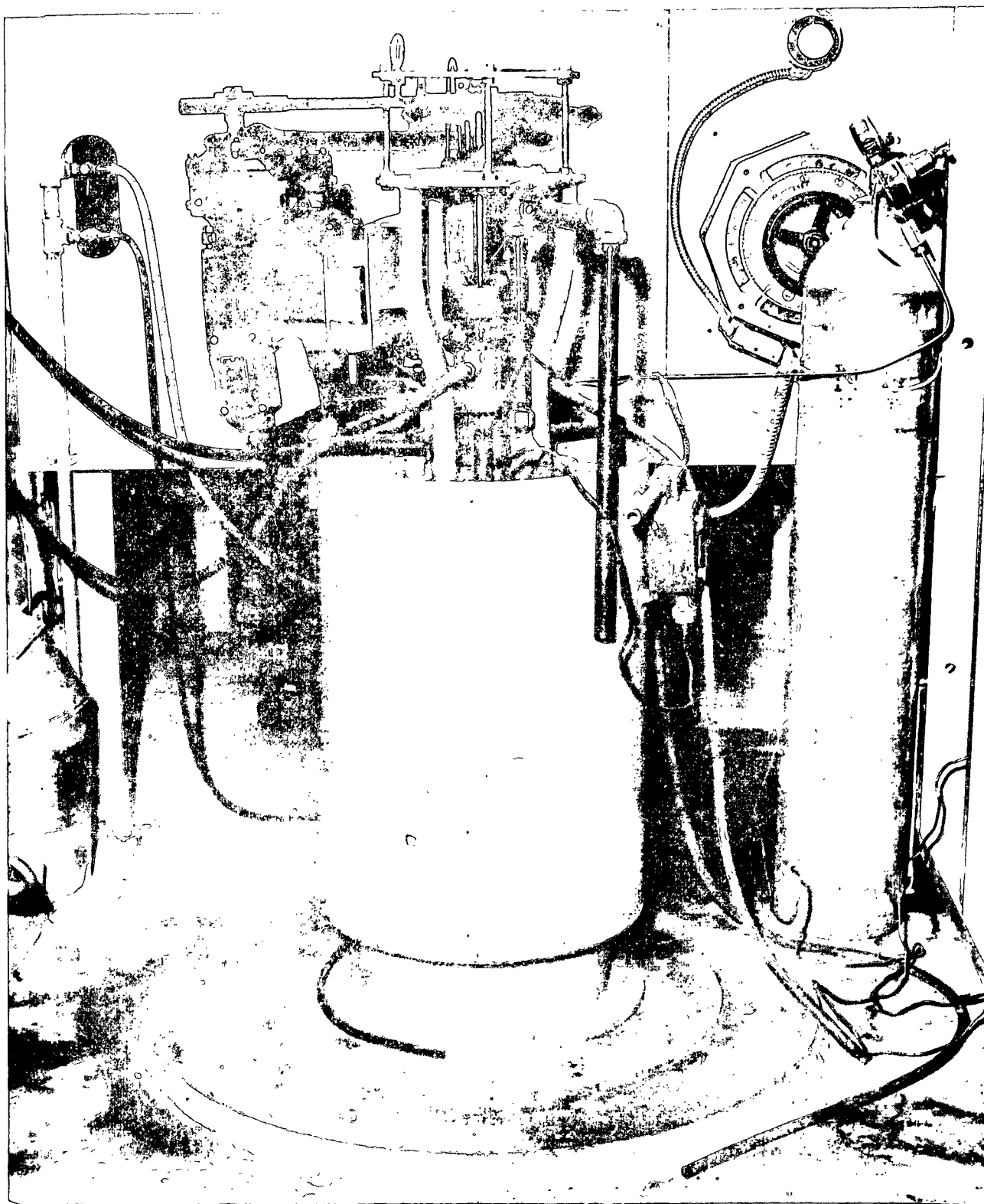


Figure 2. Pressure Vessel No. 1

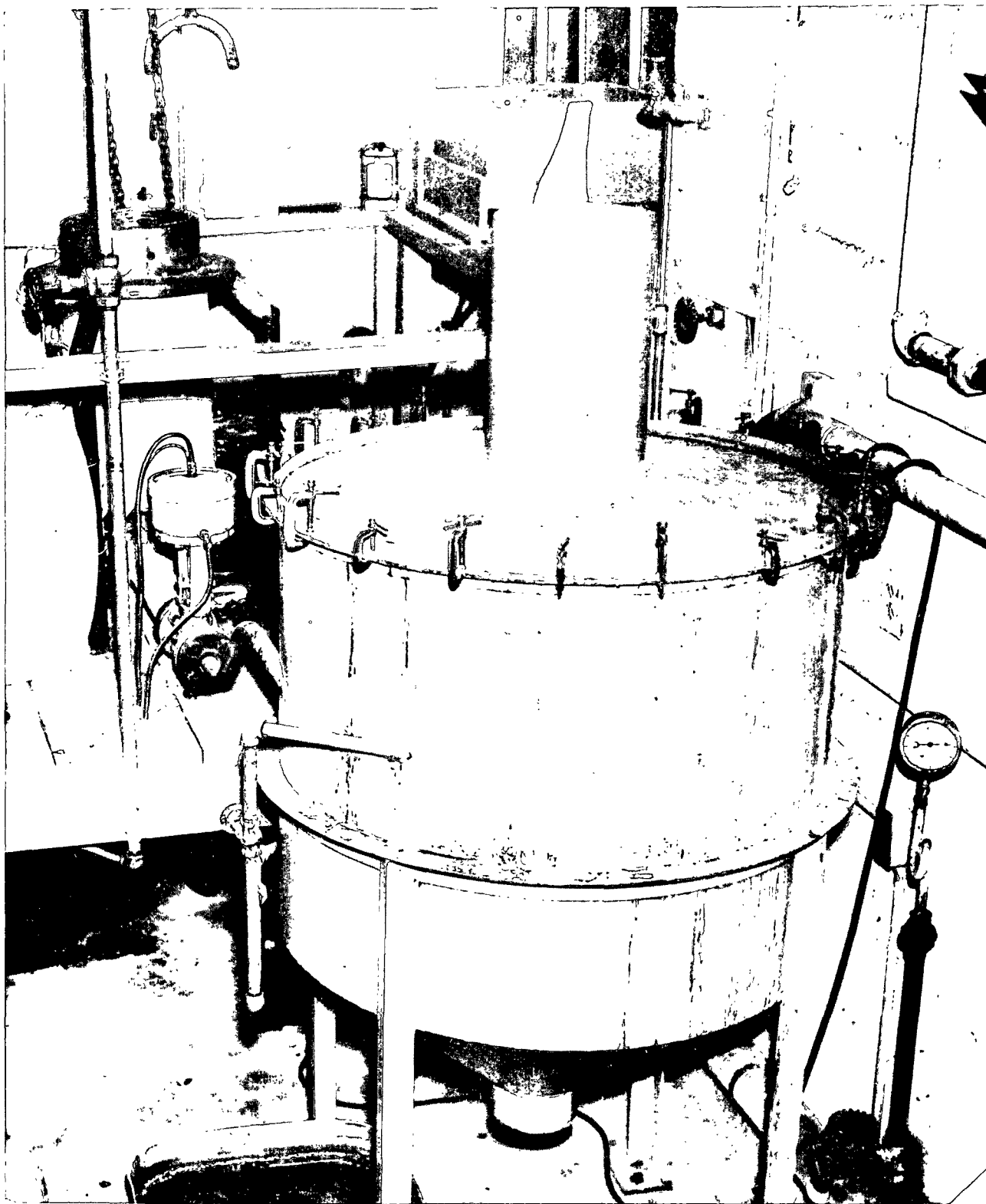


Figure 3. Cyclone Blowpit and Pressure Vessel No. 2

and a switching arrangement was built into the equipment to enable transfer of various thermocouple potentials to the potentiometers.

Liquid temperature in the preheater was measured by a thermocouple¹ inserted in an oil-filled well that was submerged in the cooking liquor. The shell wall temperature of Vessel No. 2 was measured by five thermocouples¹ appropriately spaced over the vessel (Figure 1). These thermocouples were embedded 1/4 to 1/2-inch in the vessel shell metal.

The four thermocouples² used to measure cooking temperature were specially noteworthy with respect to design and location. These thermocouples (Figure 4) were specifically constructed so as to possess a minimum heat capacity, and, when used with a rapid-response-recording potentiometer, measurement of a temperature change was extremely rapid. The design of the chip basket permitted the insertion of these four thermocouples directly into the mass of the veneer chips (Figure 5).³

All the thermocouples in the isothermal digester were calibrated to within $\pm 0.25^{\circ}\text{C}$. by the following technique. A large copper block (six by six by two inches) was appropriately drilled so as to contain a standard thermometer and one thermocouple at approximately the same

¹ These thermocouples were all made from identical wire and their potential was measured through use of the Cambridge instrument. !

² These thermocouples were all made from identical wire and their potential was measured through use of the Brown instrument.

³ See page 112.

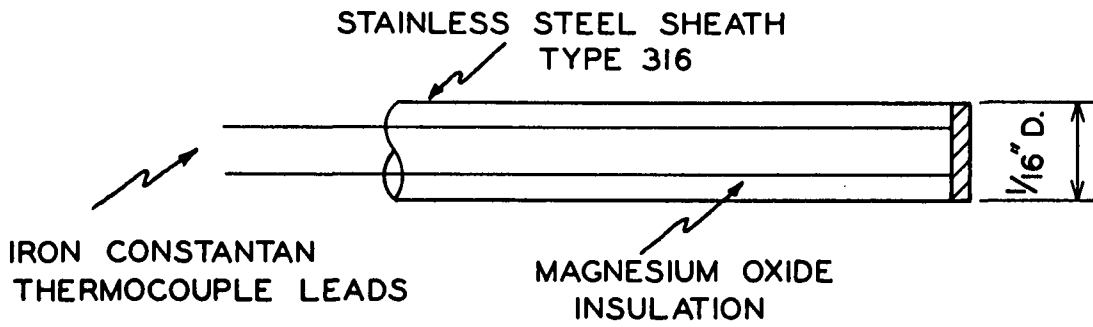


Figure 4. Ceramo Thermocouple Design

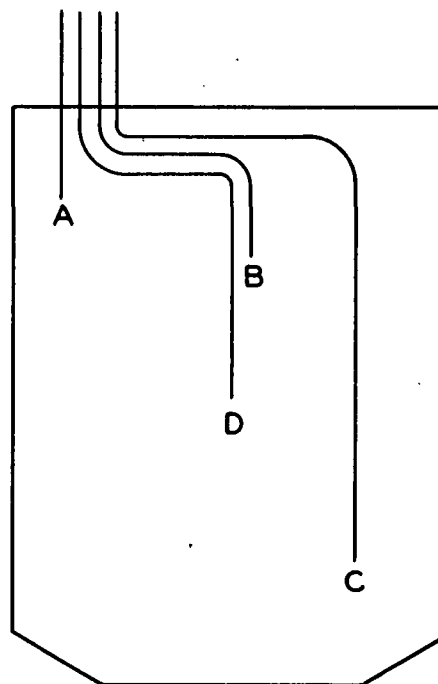


Figure 5. Thermocouple Location in Vessel No. 2

location within the block. This block was heated or cooled very slowly (about 1°C. for every five-ten minutes) and thermocouple potential was compared with the standard thermometer. This calibration was checked periodically throughout the experimental phase of the thesis.

ISOTHERMAL DIGESTER OPERATION

To obtain the desired pulping conditions in the isothermal digester, certain operational procedures had to be carefully followed. Deviation from these procedures resulted either in cooks that had a relatively long period of heat-up, or considerable temperature change occurred during pulping.

In cooking, Vessels No. 1 and No. 2 had to be heated to different temperatures. When both vessels were heated to the same temperature, it was found that a continued slow increase in cooking temperature occurred during the first five to seven minutes of pulping. The most desirable operation of the isothermal digester was obtained when the liquor was preheated to a temperature considerably higher than the final cooking temperature. The shell wall of Vessel No. 2 had to be preheated to a temperature lower than either Vessel No. 1 or the end cooking temperature desired. The actual amount of temperature difference that had to be maintained between vessels in this preheating stage had to be determined by trial and error procedures.

At time zero, the line connecting the two vessels was opened, allowing the hot liquor to transfer from Vessel No. 1 to Vessel No. 2. This

transfer occurred very rapidly because of the large pressure differential existing between the two vessels. As transfer occurred, the cooking liquor was cooled due to flashing and heat loss to Vessel No. 2 and its contents. This heat transfer in turn elevated the temperature of Vessel No. 2 to the proper level. With proper temperature manipulation in preheating, the end result was that the entire chip mass was quickly heated to the desired pulping temperature.

During such a transfer, the temperature of the wood within Vessel No. 2 rose from 50°C. to within three degrees of cooking temperature during the first 10 seconds. In the next 20 seconds, the temperature rose to within one degree of cooking temperature, and 40-45 seconds after transfer, the final cooking temperature was reached. The desired pulping temperature could be achieved within $\pm 1^{\circ}\text{C}.$, and during cooking it was possible to control to that temperature within $\pm 1^{\circ}\text{C}.$ Therefore, the over-all reproducibility of the isothermal digester was approximately $\pm 2^{\circ}\text{C}.$, with extremely careful operation narrowing this deviation to about $\pm 1.5^{\circ}\text{C}.$ Temperature measurements at four different points in the wood charge showed that at any given time, the temperature variation throughout the chip charge did not exceed $1^{\circ}\text{C}.$

Throughout the cooking cycle, Vessel No. 1 was always maintained at its original high temperature, while Vessel No. 2 was maintained at cooking temperature. Hence, a temperature difference between vessels existed, and this temperature difference was responsible for a considerable vapor pressure differential between vessels. This pressure differential

kept Vessel No. 2 filled with cooking liquor and prohibited any back-transfer of liquor.

Quenching, which was accomplished by blowing the entire liquor contents of both vessels to the atmosphere through a cyclone blowpit, caused the temperature to drop 70-80°C. during the first ten seconds. As the temperature fell to about 100°C., cold water was injected into the digester, completing the quenching cycle by reducing the temperature to about 30°C. Figure 6 is a duplication of a recorded temperature profile obtained from a typical cook. This temperature profile was made by a continuous recording of thermocouple D, which was located in the geometric center of the chip mass. Such data involve a slight inaccuracy, as both the recording instrument and the thermocouple slightly lag the actual temperature change. The effect of this lag period is to de-emphasize the rate of temperature change. However, even the measured rate of temperature change showed that the isothermal digester did meet the experimental requirements within certain limits. It was felt that for cooks of less than three minutes duration, there was no great degree of precision, and the minimum meaningful cooking time was approximately 90 seconds.

One difficulty that was expected but did not occur in operation of the isothermal digester was a shattering of the fiber cell wall by explosion during quenching. Stone (24) showed that wood loses much of its strength as its temperature is increased. Furthermore, in this thesis, additional softening of the wood structure would be expected because of the pulping action. Thus, at the time of the blow, the walls

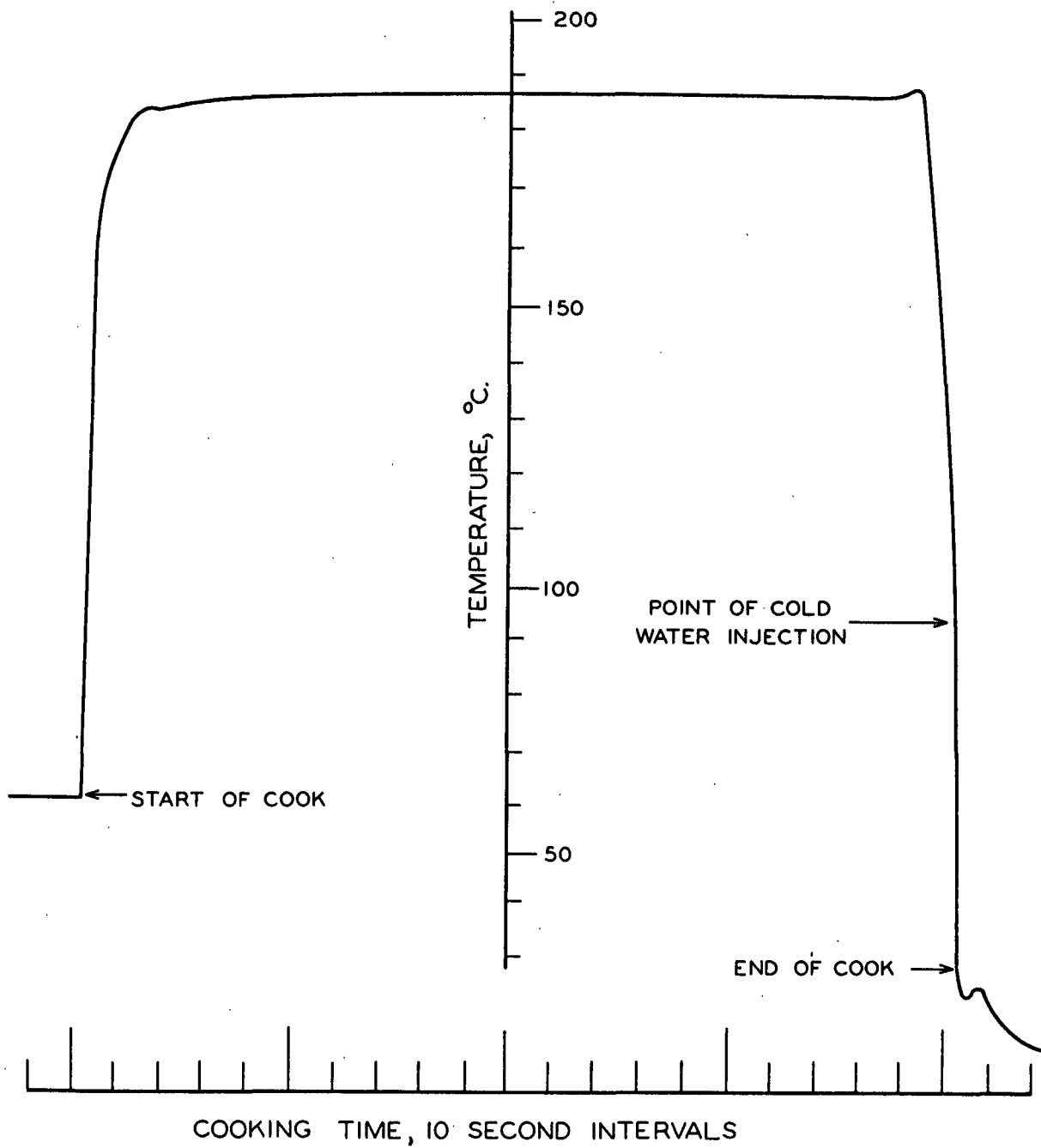


Figure 6. Measured Temperature Curve. Cook 34

of the individual fiber cells are in a very soft and pliable condition. These cells are filled with liquor at a temperature equivalent to that of the cook. With the external pressure being removed, it seemed reasonable to assume that the individual cells might be exploded by the rapid vaporization of the liquor trapped within the cells. This explosion of the individual cells would be very similar to the defibering action which occurs in the Masonite process. However, microscopic examination of the pulps produced no evidence of any shattering of the cell wall. In fact, during blowing, all the pulp remained in the basket in its original physical structure. It was only when mechanical action was applied to the "softened" chips that defibering occurred. The results were the same even when pulps were cooked to a yield of 44%; hence, there was no evidence of physical damage to the fibers resulting from the blowing procedure, and no significant loss of fiber from the basket.

OUTLINE OF THE EXPERIMENTAL PROGRAM

Preliminary cooks with the isothermal digester delimited the temperature range which could be investigated. Temperatures below 170°C. were of little interest because of the exceedingly low rates of reaction associated with these temperatures.

The upper limit of investigation was fixed by a combination of two factors. The isothermal digester was designed for a maximum operating pressure of 1000 p.s.i.a. This pressure was achieved when pulping at 230°C., thereby establishing the maximum temperature which would be investigated. (To cook at 230°C., Vessel No. 1 had to be preheated to 260°C., which in turn determined the over-all operating pressure.)

The second factor establishing the upper temperature range was the minimum meaningful cooking time that could be reproduced by the isothermal digester. As reaction rates increase, cooking time must be reduced. Experimentation showed that at temperatures of 215-220°C., reaction rates were sufficiently high to make it impossible to obtain yields above 60% in the minimum meaningful cooking time (90 seconds) of the isothermal digester. Reproducible cooks of three minutes or more at these same temperatures reduced pulp yields to about 50%. Hence, it was felt that 210°C. represented the upper temperature limit at which the isothermal digester could operate in a precise manner, and still produce yields of interest to the papermaker.

With the temperature range delimited, the following cooking schedule was used as the basis of the experimental program. "Isothermal" cooks were made at four temperature intervals (173, 186, 200, and 210°C.). At each temperature, five pulps were produced. The pulping time of each cook was varied so as to space pulp yields between 45 and 75%. No attempt was made to pulp to a precise yield figure, as this would have involved tedious trial-and-error techniques in the determination of cooking times.

The chemical and physical properties of the pulps obtained from the cooking program were investigated according to a standardized procedure. The sequence of tests used is best described by a schematic diagram (Figure 7), and the details of each test procedure can be found tabulated in the Appendix (page 114).

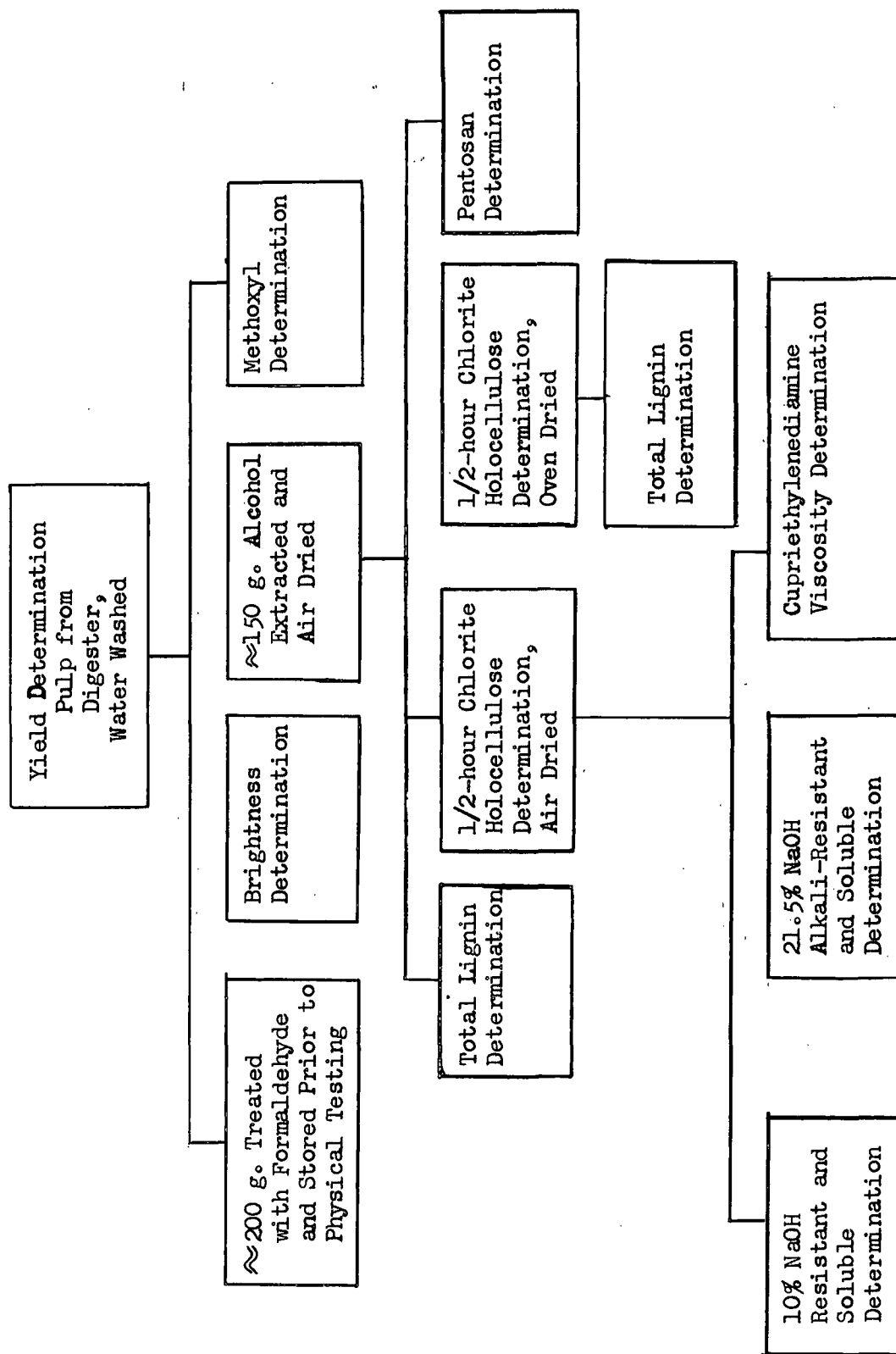


Figure 7. Schematic Drawing, Chemical Analysis

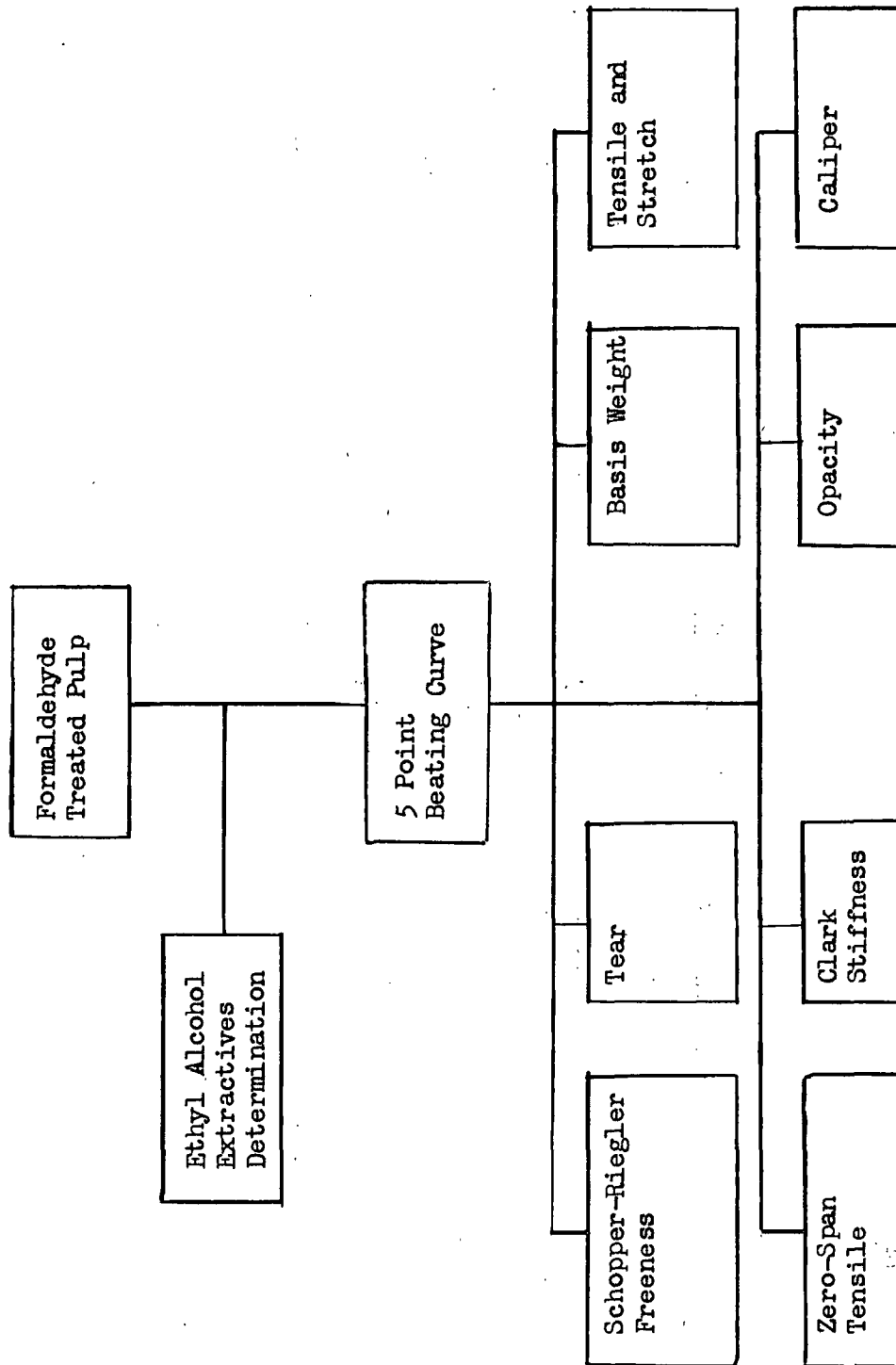


Figure 7 (continued). Schematic Drawing, Physical Analysis

WOOD PREPARATION

Seven aspen (Populus tremuloides) trees were selected and cut from the Rhinelander Experimental Forest. All of these trees were located on the same site, and had a diameter of at least 10 inches at breast height (Table II). Two 48-inch logs were removed from the trunk of each tree, and the logs were cut into sheets 0.023 inches thick (35-40 fibers in cross section) on a commercial veneering lathe. The cutting operation was so adjusted that only sapwood was utilized, and sheet thickness was held to within ± 0.001 inches. The thickness showed no measurable change upon drying of the wood.

The veneering sheets obtained from the logs were air dried and stored for a period of six months. Following storage, the sheets were cut into one-inch ribbons (± 0.1 inch) with a guillotine-type paper cutter. The orientation of the sheets at cutting was such as to align the grain of the wood perpendicular to the cutting edge.

The one-inch ribbon of wood veneer was hand-broken into approximately one-inch squares (see Figure 8). These one-inch squares were thoroughly blended and weighed out into individual cook charges. Each charge was stored in a polyethylene bag until used in pulping.

TABLE II

GROWTH CHARACTERISTICS OF ASPEN EXPERIMENTAL LOGS

Log No.	Log Age, growth ring count	Heartwood Age, growth ring count	Av. Log Diameter, inches	Av. Heartwood Diameter, inches
1	46	21	11-5/8	4-5/8
2	44	21	11-2/8	4-5/8
3	42	20	12-6/8	5-2/8
4	47	21	10-5/8	5
5	49	26	11-4/8	5-4/8
6	36	18	10	5-3/8
7	43	18	11-5/8	5-3/8
8	36	17	9-4/8	4-5/8
9	48	28	11-4/8	5-2/8
10	41	18	11-5/8	5
11	46	18	12-3/8	5

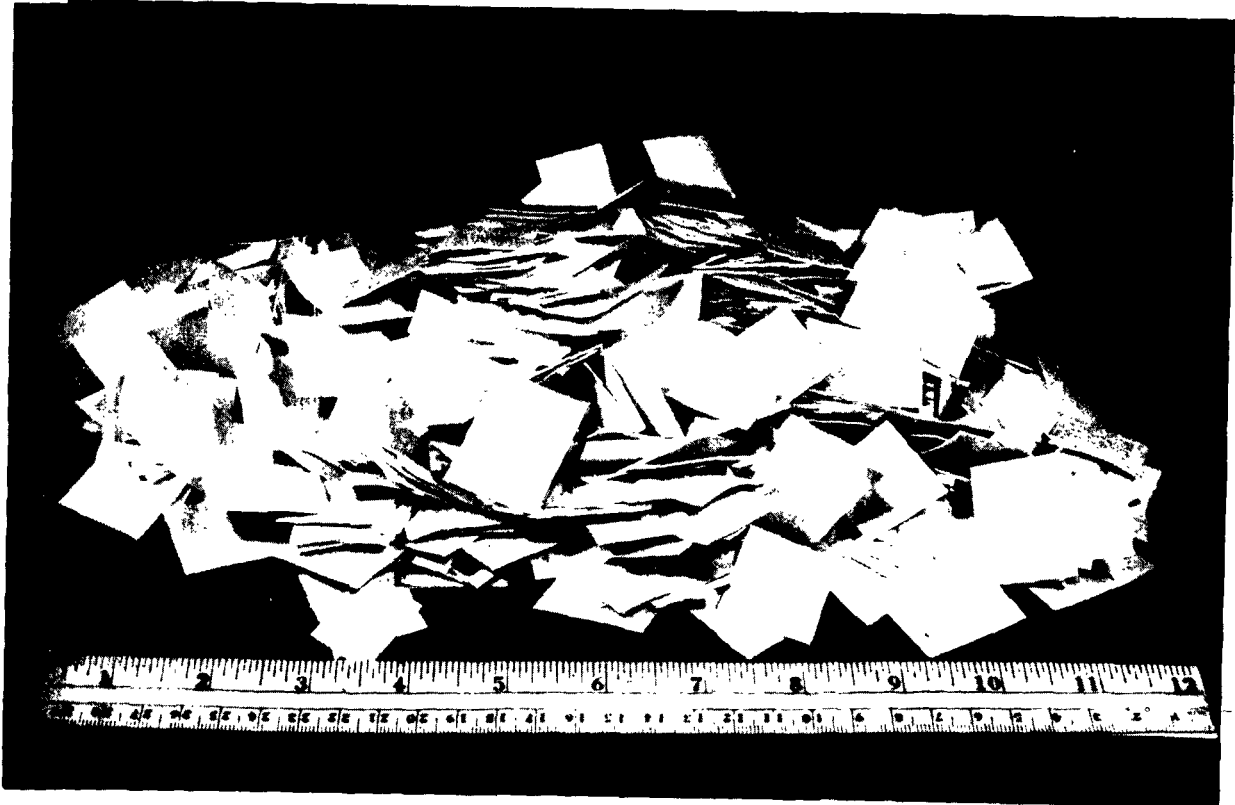


Figure 8. Veneer Chips Used in Cooking

EXPERIMENTAL RESULTS

TEMPERATURE CORRECTION

One of the basic aims of the experimental program was to obtain series of pulps cooked at the same pulping temperature, with cooking time being varied to produce certain desired yields. Several such isotherms were obtained, thereby yielding relationships between cooking time, temperature, and yield.

While the experimental pulping equipment was designed to approach isothermal conditions, temperature variations of about $\pm 2^{\circ}\text{C}$. did occur during cooking. Also, a small but finite time was required to heat and quench the digester. It was desirable to correct for these small temperature variations by mathematically adjusting the cooking time to a value equivalent to a cook conducted under precisely isothermal conditions. Through an empirical approach, a method to make such corrections was developed.¹

The calculated equivalent cooking time for each experimental cook was determined, and can be seen in Table III. If the experimental conditions had been truly isothermal, the equivalent and actual cooking time would have been identical. Therefore, the difference between equivalent and actual cooking time is a measure of the amount of temperature variation that existed in the cook. Comparisons of these values show that experimental conditions did approach the ideal isothermal experiment.

¹ Appendix, page 123

TABLE III

COOKING TIME

Cook No.	Temperature of Pulping, °C.	Yield, % ^a	Actual Cooking Time, sec.	Equivalent Cooking Time, sec.
32	173°	81.7	430	397
31	173°	72.3	2,020	1,922
29	173°	71.3	1,995	1,961
39	173°	62.7	4,260	4,048
33	173°	50.8	14,410	14,556
34	186°	75.1	190	172
36	186°	66.1	610	703
35	186°	61.9	1,630	1,642
38A	186°	54.3	3,610	3,282
37	186°	44.0	6,110	6,495
40	200°	74.5	100	118
42	200°	68.9	240	222
43	200°	61.8	520	457
44	200°	51.7	1,460	1,422
41	200°	44.1	2,650	2,598
47	210°	68.2	90	84
46	210°	64.6	160	149
49	210°	60.1	310	303
48	210°	50.3	550	560
45	210°	43.9	970	896

^a Yield expressed in percentage of oven-dry wood.

It was felt that the calculated equivalent cooking time represented the most meaningful measurement of total pulping time, and, hence, equivalent cooking time was used throughout this thesis in plotting time-temperature relationships.

YIELD

Pulp yield was determined according to standard procedures¹, and the data obtained can be found in Table III. In order to illustrate the relationship of time-temperature-yield, a plot of yield versus the logarithm of equivalent cooking time is shown in Figure 9. The purpose in using the logarithmic function was simply to reduce the time scale to reasonable proportions.

It is interesting to note the similarity in curvature between the isotherms obtained; these data indicate the similarity in the pulping process with increasing cooking temperature. However, it should also be noted that increasing pulping temperature greatly affects the time required to produce any given yield. The use of the logarithmic time scale in Figure 9 tends to de-emphasize this extremely important effect of temperature.

LIGNIN CONTENT

Klason lignin and ultraviolet measurements (UV) of the soluble lignin in the Klason filtrate were made according to standard Procedures²,

¹ Appendix, page 114

² Appendix, page 117

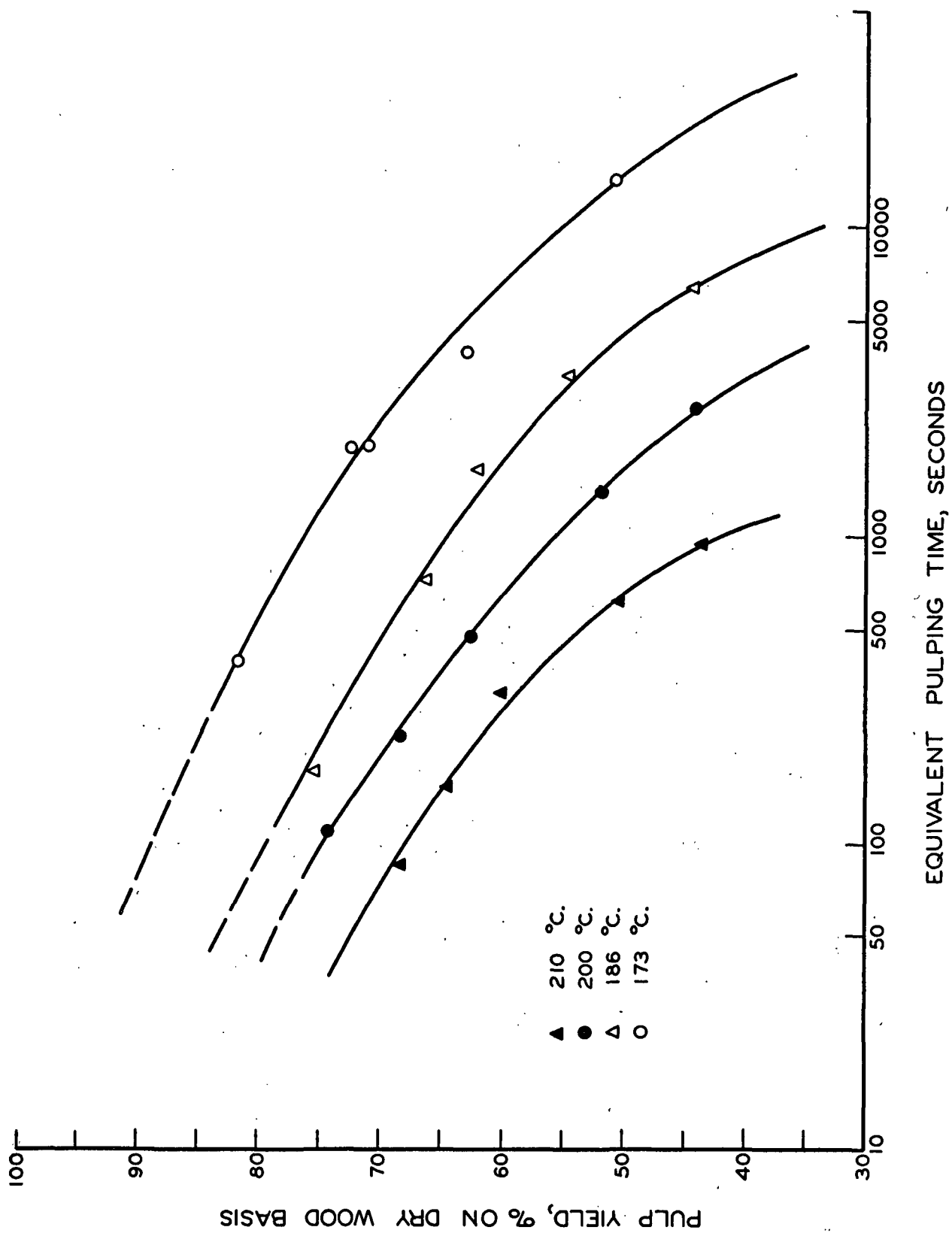


Figure 9. Pulp Yield vs. Log Equivalent Pulping Time

and the sum of the two was termed "total lignin". The values obtained can be found tabulated in Table IV expressed on the wood basis. The effect of pulping temperature on lignin content is most apparent in a plot of total lignin versus yield (Figure 10). This figure shows that increasing pulping temperature tended to slightly increase the amount of lignin remaining in the pulp when comparisons are made at equal yields. However, the indicated trends in change of lignin content with pulping temperature must be considered with some skepticism. The temperature effect observed was small, as a 37°C. change in pulping temperature altered total lignin content at a given yield only by about 1% in the 50-60% yield range. Whether such a small change in lignin content could be definitely established by the testing procedures employed is open to some question, so the data obtained must be considered as only indicating a possible trend.

METHOXYL CONTENT

When one considers the precision and accuracy of the total lignin determination, and compares it to the minor differences apparently related to pulping temperature, the significance of this difference becomes questionable. It, therefore, becomes very desirable to support the trends shown in the total lignin content by some other test procedure. Methoxyl determinations¹ were made on all the pulps, and the information obtained can be found on Table IV. In pulp, the majority of the methoxyl groups should be contained within the structure of the lignin, and, hence, methoxyl content can be assumed to be related to lignin

¹ Appendix, page 115

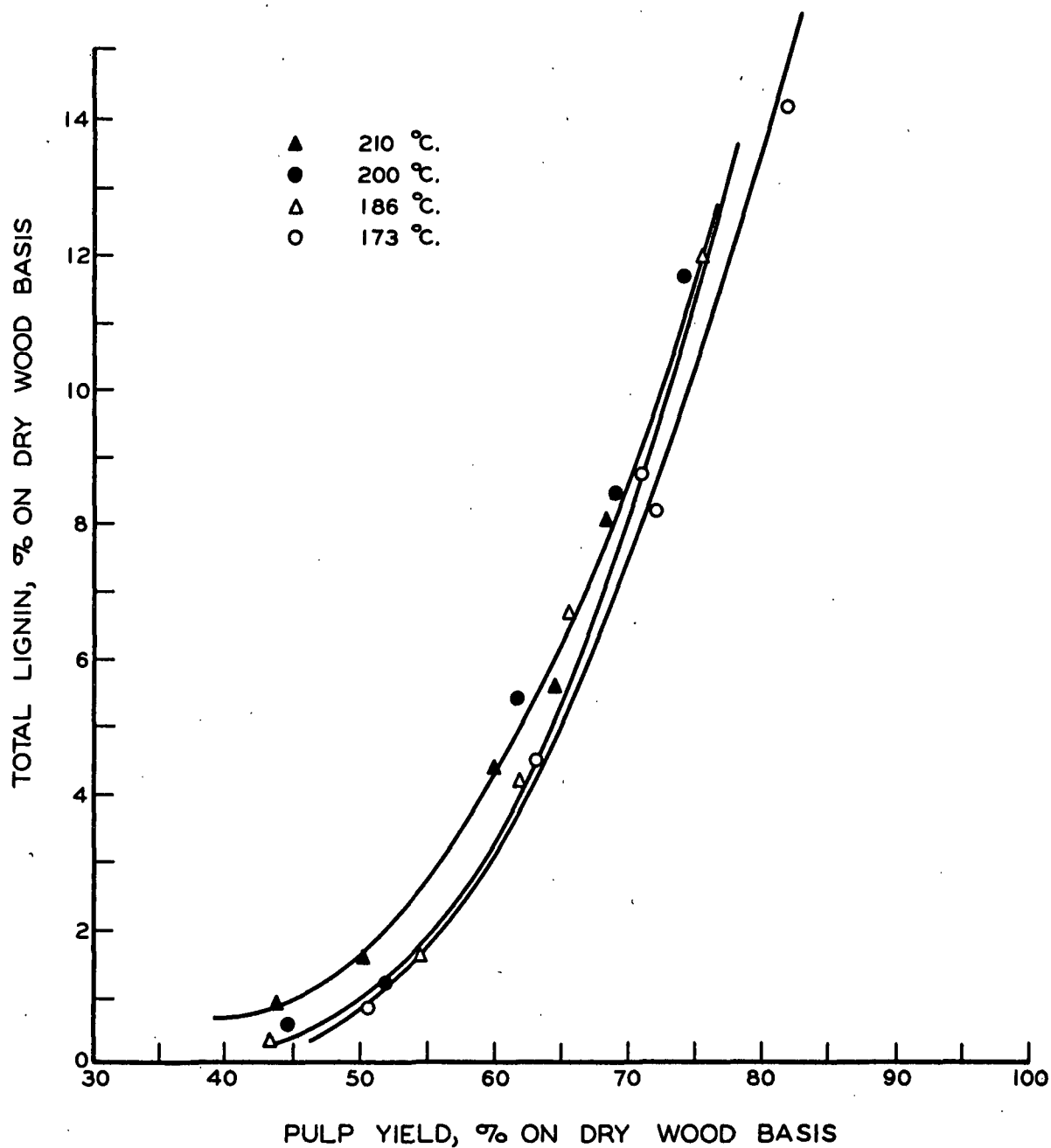


Figure 10. Total Lignin vs. Pulp Yield

TABLE IV

CHEMICAL ANALYSIS

Cook No.	Temperature of Pulping, °C.	Yield, %	Equivalent Cooking Time, seconds	Klason Lignin, %	Ultra- violet Lignin, %	Total Lignin, %	Methoxyl Content, %	Extrac- tives, %	Holo- cellulose, %
32	173	81.7	397	10.1	4.1	14.2	3.62	1.7	64.7
31	173	72.3	1922	5.6	2.6	8.2	2.11	1.4	61.2
29	173	71.3	1961	6.0	2.7	8.7	2.24	1.4	60.2
39	173	62.7	4048	2.6	1.8	4.4	1.17	1.1	56.3
33	173	50.8	14556	0.3	0.6	0.9	0.29	0.9	48.3
34	186	75.1	172	8.1	3.7	11.8	2.93	1.7	61.4
36	186	66.1	703	4.5	2.2	6.7	1.77	1.8	57.4
35	186	61.9	1642	2.6	1.6	4.2	1.15	1.5	55.5
38A	186	54.3	3282	1.0	0.6	1.6	0.48	1.0	51.3
37	186	44.0	6495	0.2	0.3	0.5	0.13	1.0	42.5
40	200	74.5	118	8.9	2.8	11.7	3.05	1.6	59.5
42	200	68.9	222	6.0	2.4	8.4	2.12	1.7	57.7
43	200	61.8	457	3.6	1.8	5.4	1.36	1.4	54.1
44	200	51.7	1422	0.8	0.4	1.2	0.39	1.0	48.6
41	200	44.1	2598	0.2	0.4	0.6	0.01	0.7	42.5
47	210	68.2	84	5.8	2.3	8.1	2.14	2.0	57.3
46	210	64.6	149	4.6	1.0	5.6	1.65	1.8	55.7
49	210	60.1	303	3.0	1.4	4.4	1.21	1.6	53.7
48	210	50.3	560	0.9	0.7	1.6	0.39	1.1	47.1
45	210	43.9	896	0.6	0.3	0.9	0.01	0.8	41.8
Wood		100.0	—	17.8	2.7	20.5	—	3.1	75.4

Note: all percentages expressed in this table are based on the oven-dry wood.

content. When the methoxyl data were plotted against pulp yield (Figure 11), it was found that methoxyl content was higher in the case of high-temperature pulps. This, of course, supports the trends shown by the total lignin data.

ALCOHOL EXTRACTIVES

The amount of alcohol extractives¹ can also be found in Table IV where it is expressed as a percentage based on the original wood. When the amount of extractives was plotted as a function of yield and pulping temperature (Figure 12), it was noticed that there was a probable relationship between temperature of pulping and amount of extractives. Increasing pulping temperature did increase the amount of material which was extractable by alcohol, but this increase was undoubtedly very small in order of magnitude (approximately 0.6 to 0.7% per 37°C. temperature change). With the 186°C. isotherm the data were too erratic to predict the isotherm's exact location.

TOTAL CARBOHYDRATE MATERIAL

A sodium chlorite holocellulose determination² was used as a measure of the total carbohydrate fraction present, and the results of this determination can be found in Table V. Figure 13 shows the relationship between holocellulose and yield with temperature as a parameter. As temperature was increased, pulps of equivalent yield contained slightly less holocellulose.

¹ Appendix, page 116

² Appendix, page 118

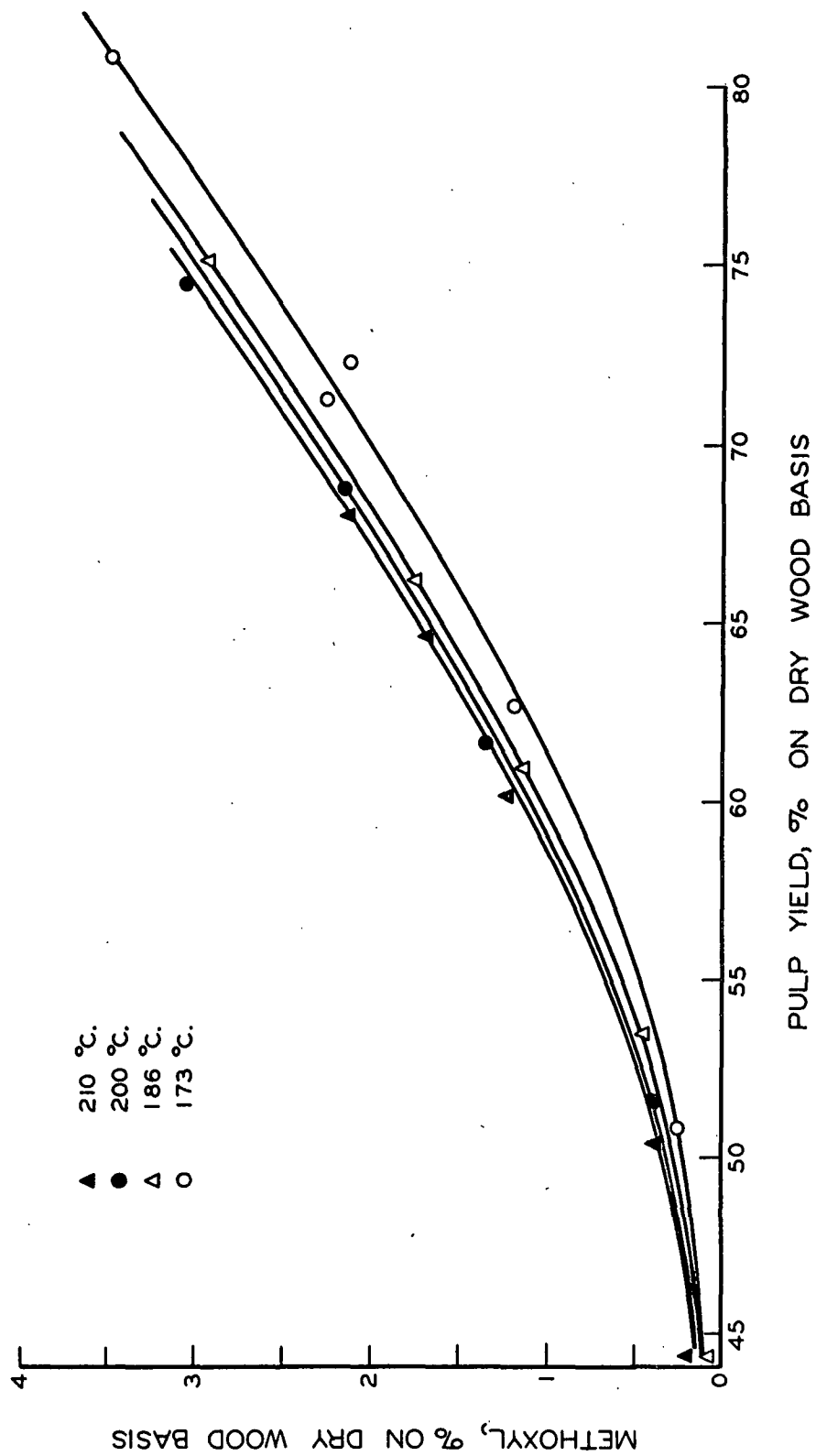


Figure 11. Per Cent Methoxyl vs. Pulp Yield

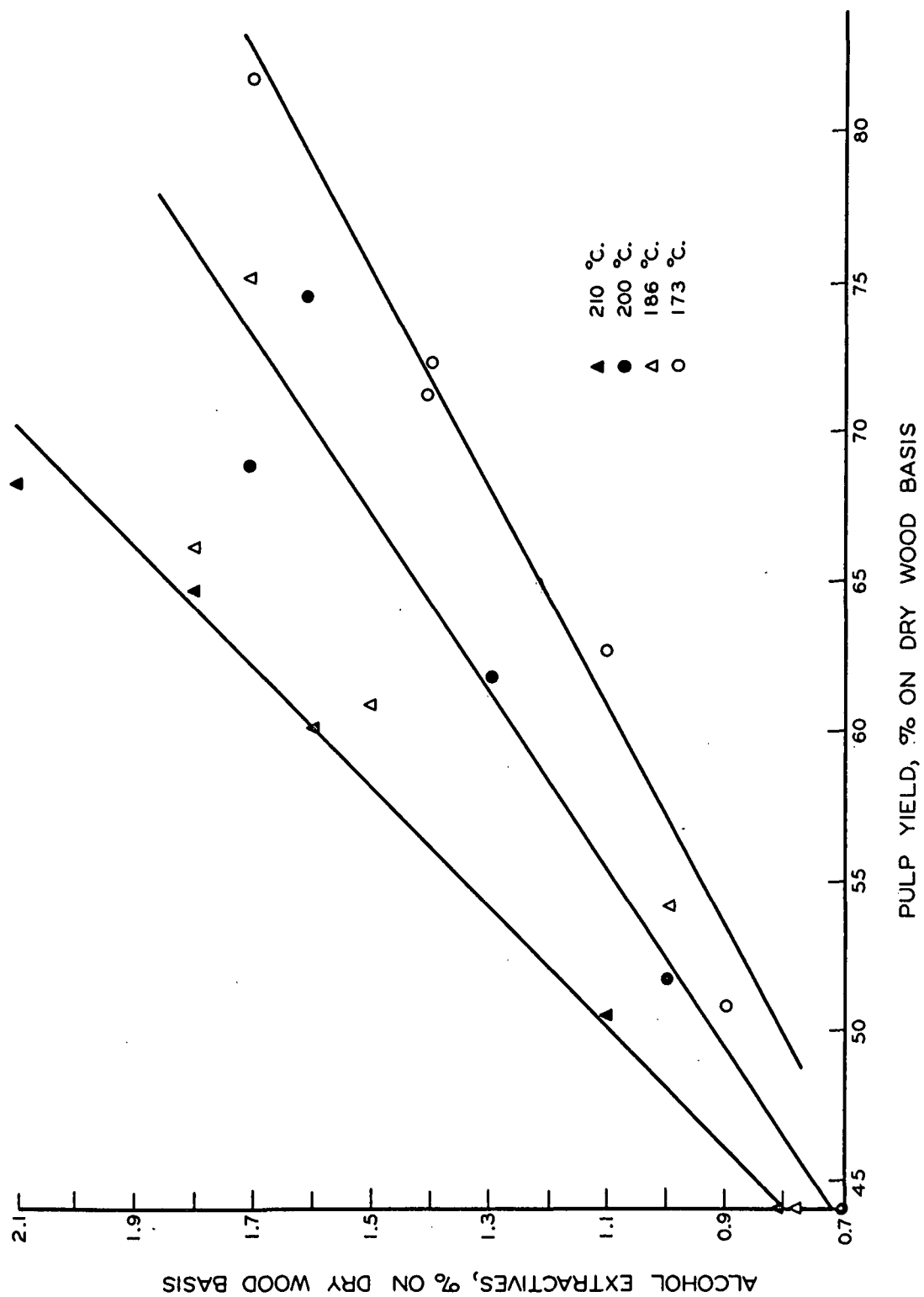


Figure 12. Alcohol Extractives vs. Pulp Yield

TABLE V

CHEMICAL ANALYSIS

Cook No.	Temperature of Pulping, °C.	Yield, %	Viscosity Determination, centipoise	Pentosan Content, %	21.5% Alkali Resistant, %	21.5% Alkali Soluble, %	10% Alkali Resistant, %	10% Alkali Soluble, %
32	173	81.7	29.5	14.6	53.9	10.8	51.5	13.2
31	173	72.3	32.0	13.0	52.8	8.4	51.0	10.2
29	173	71.3	37.7	12.6	51.4	8.8	48.5	11.7
39	173	62.7	24.4	11.5	50.4	5.9	49.4	6.9
33	173	50.8	8.8	8.0	42.9	5.4	41.5	6.8
34	186	75.1	--	12.1	53.2	8.2	51.1	10.3
36	186	66.1	22.3	10.7	51.4	6.0	50.2	7.2
35	186	61.9	16.4	9.9	49.6	5.9	48.4	7.1
38A	186	54.3	10.6	8.2	46.4	4.9	44.9	6.4
37	186	44.0	3.9	5.9	37.8	4.7	35.9	6.6
40	200	74.5	36.9	11.5	51.9	7.6	50.6	8.9
42	200	68.9	26.7	10.1	51.4	6.3	50.1	7.6
43	200	61.8	18.0	9.3	49.1	5.0	48.0	6.1
44	200	51.7	6.7	7.0	44.6	4.0	43.2	5.4
41	200	44.1	3.8	5.2	38.5	4.0	36.4	6.1
47	210	68.2	17.2	9.1	51.2	6.1	50.1	7.2
46	210	64.6	15.0	8.7	50.6	5.1	49.5	6.2
49	210	60.1	12.6	8.2	48.8	4.9	47.8	5.9
48	210	50.3	4.8	6.4	43.4	3.7	41.5	5.6
45	210	43.9	3.3	4.8	36.4	5.4	35.0	6.8
Wood		100.0	--	18.7	64.9	10.5	61.7	13.7

Note: All percentages in this table are expressed on the dry wood basis.

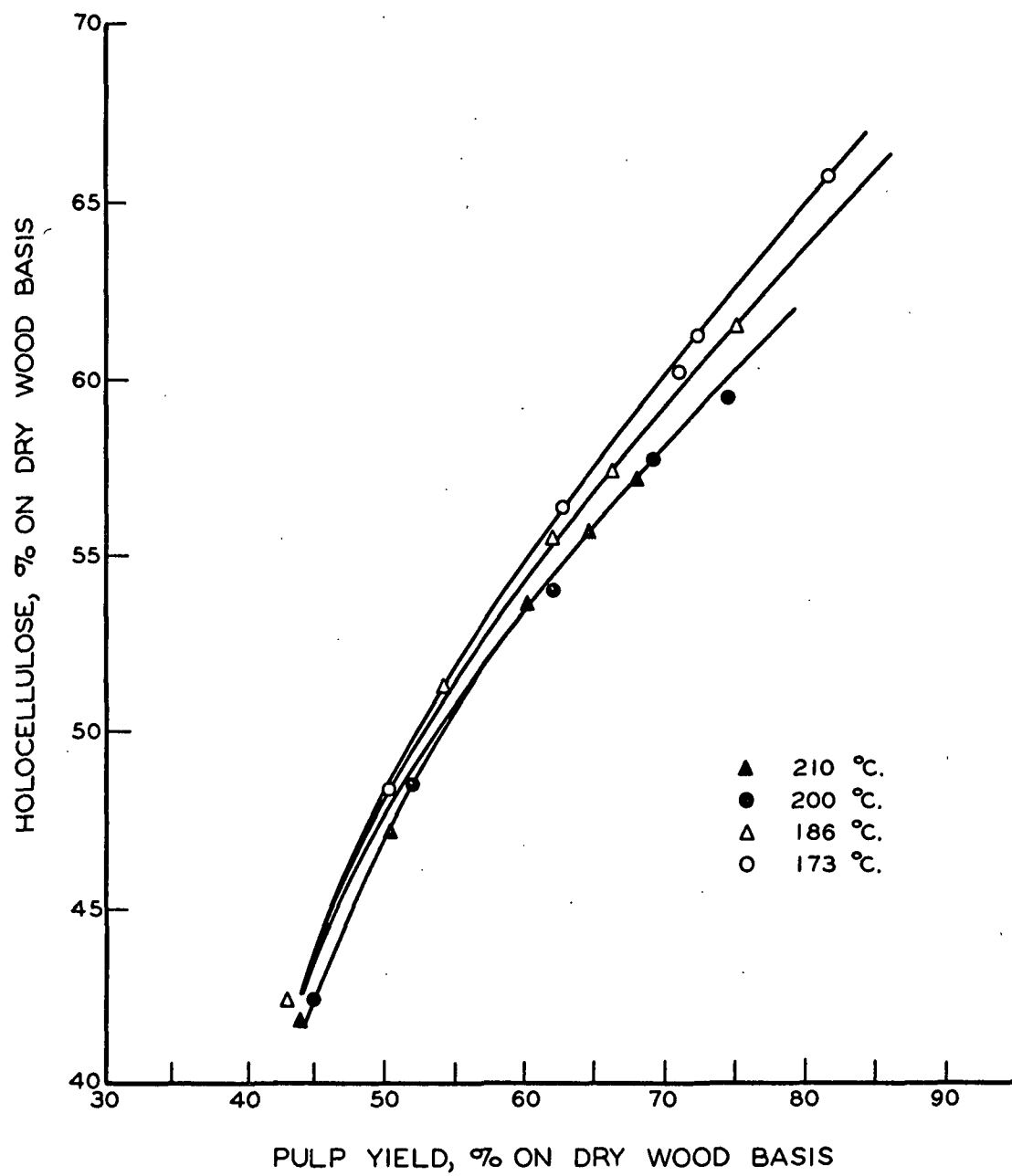


Figure 13. Per Cent Holocellulose vs. Pulp Yield

ALKALI-RESISTANT CELLULOSE

Specially prepared holocellulose pulps were treated with 10 or 21.5% sodium hydroxide solutions¹. The material which remained undissolved in the alkaline solution was termed 10 or 21.5% alkali-resistant cellulose, respectively. Similarly, the material which dissolved in the alkali was termed 10 or 21.5% soluble carbohydrate.

The measured values for alkali-resistant cellulose and soluble carbohydrate material based on the wood can be found in Table V. These values were plotted as a function of yield, and the respective plots can be found in Figures 14, 15, 16, and 17. Comparisons of the curves show that there was little, if any, temperature effect on the amount (based on the wood) of alkali-resistant cellulose. The amount of soluble carbohydrate material, however, showed changes with temperature of pulping. When comparisons were made at the same yield, increasing pulping temperature resulted in pulps containing a lower per cent of alkali-soluble carbohydrate material. The concentration of alkali in the test affected the absolute value of the soluble material, but the relative effect of temperature remained approximately constant for both 10 and 21.5% alkali.

PENTOSAN

Pentosan determinations were conducted on the pulps according to standard procedures², and these results can be found in Table V. When

¹ Appendix, page 119

² Appendix, page 116

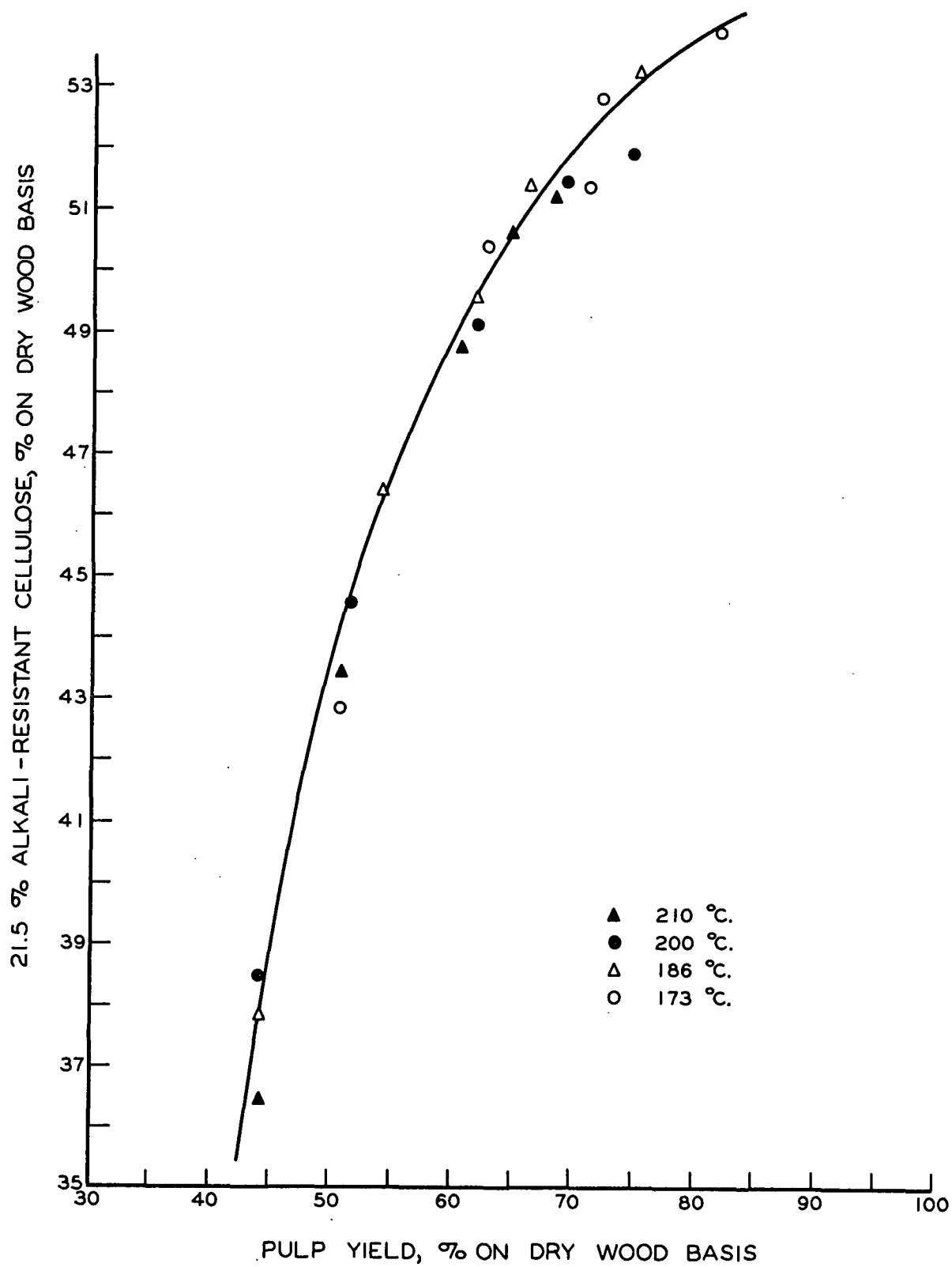


Figure 14. 21.5% Alkali-Resistant Cellulose vs. Pulp Yield

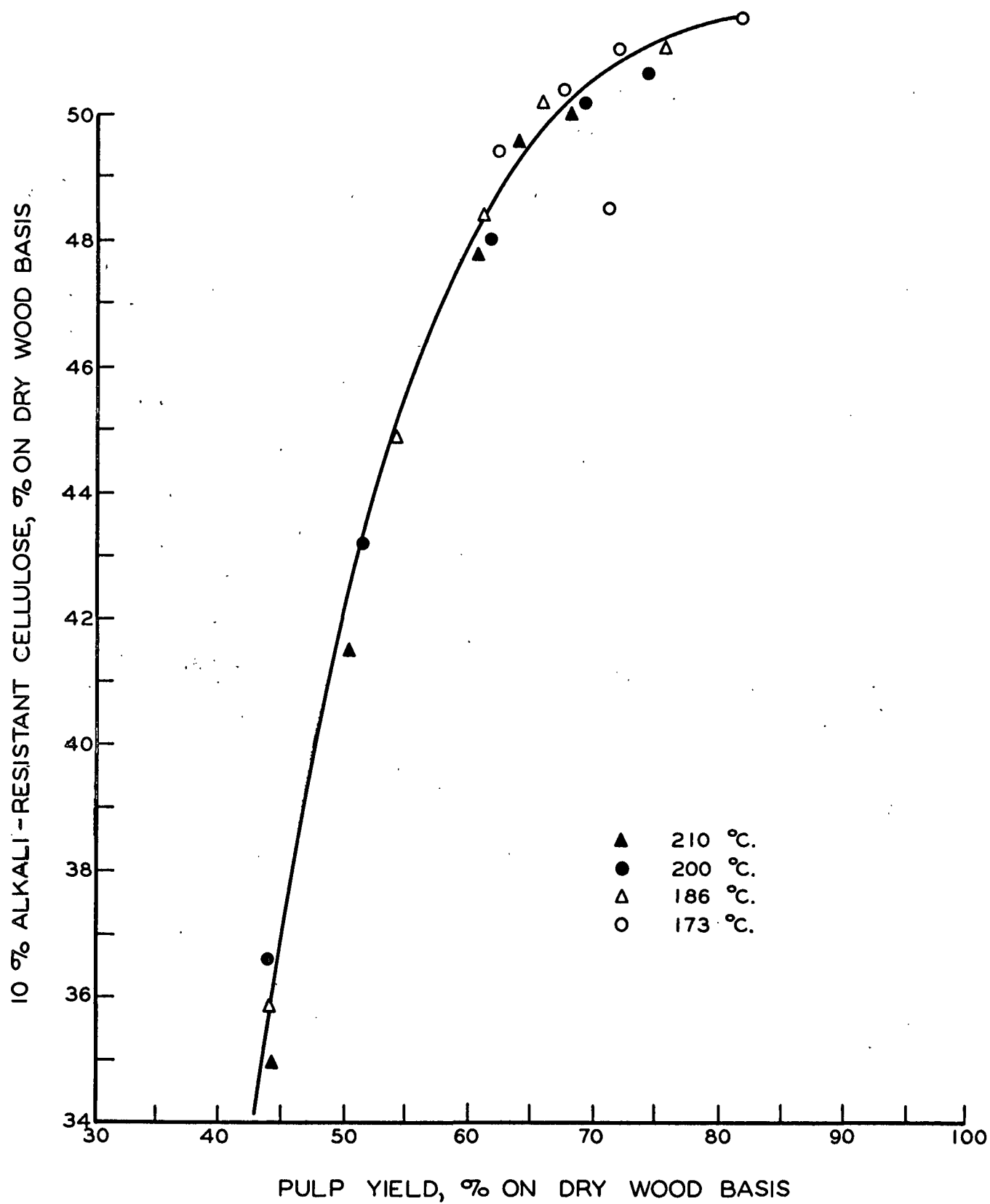


Figure 15. 10% Alkali-Resistant Cellulose vs. Pulp Yield

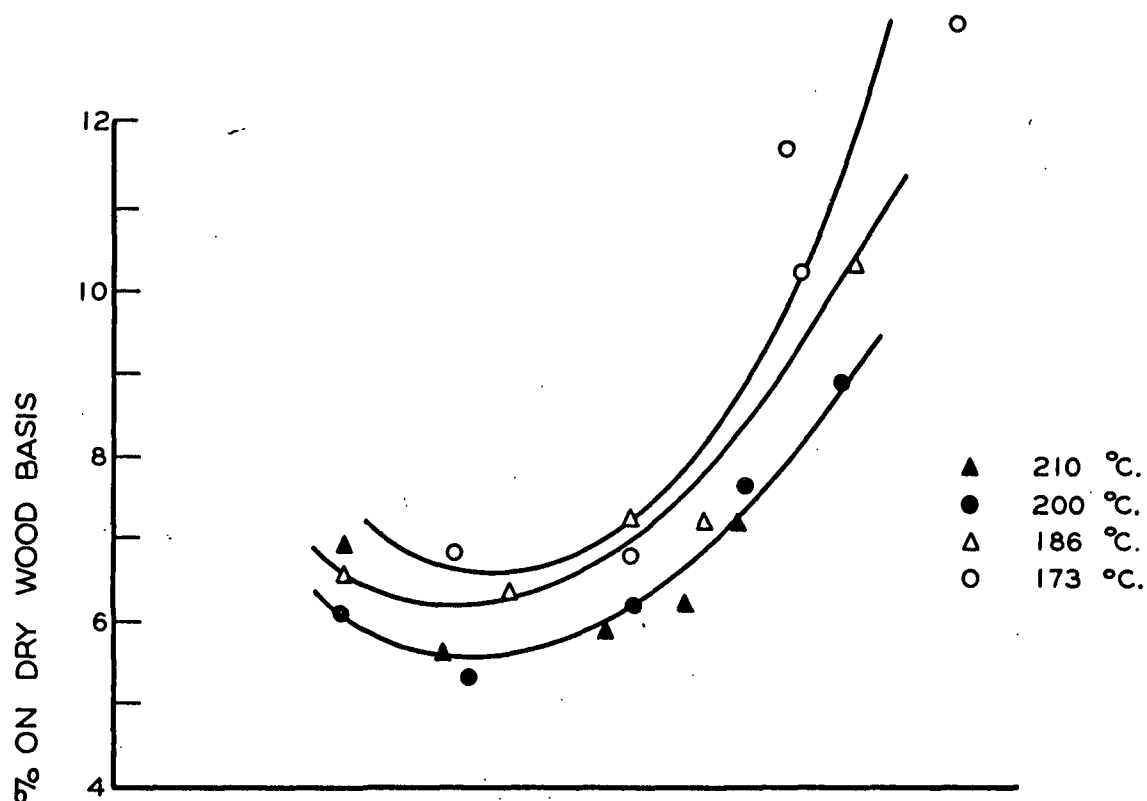


Figure 16. 10% Alkali-Soluble Material vs. Pulp Yield

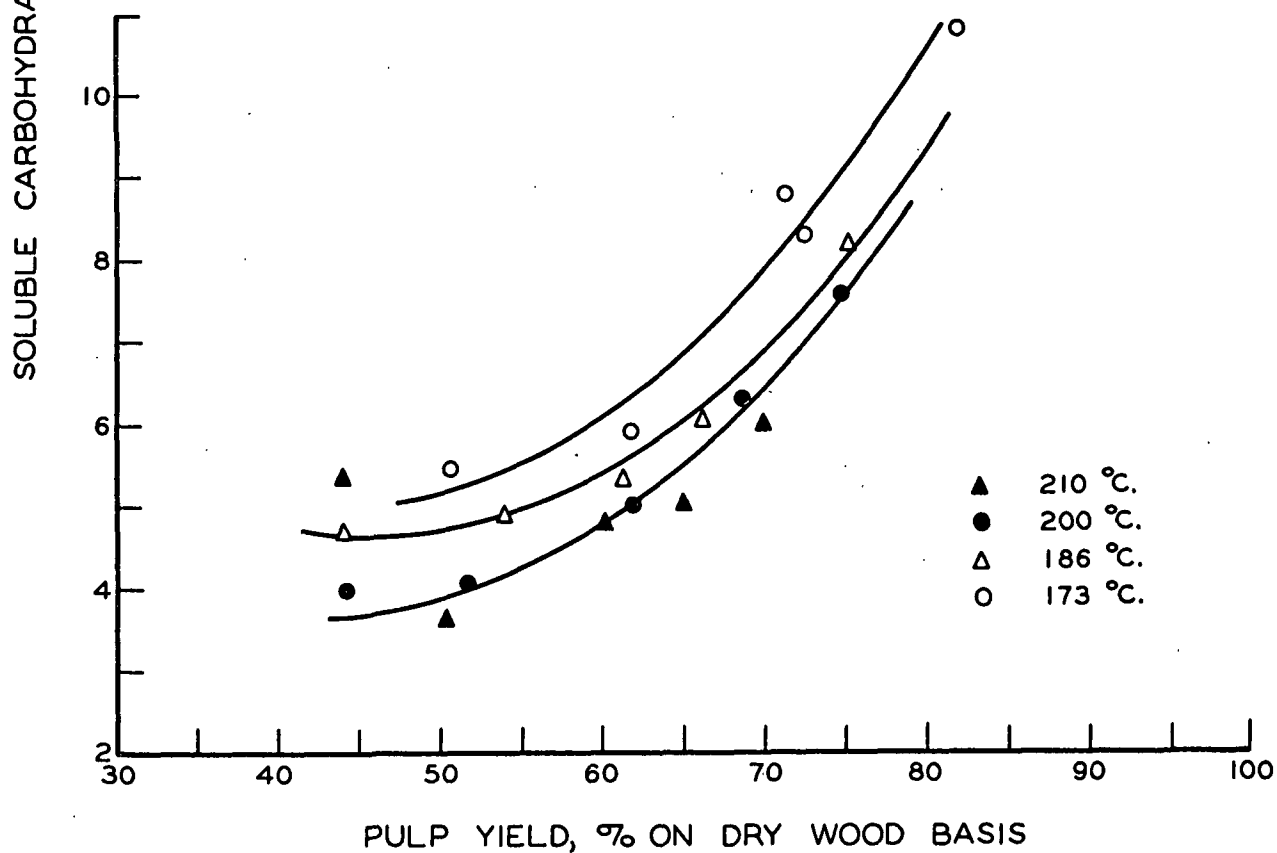


Figure 17. 21.5% Alkali-Soluble Material vs. Pulp Yield

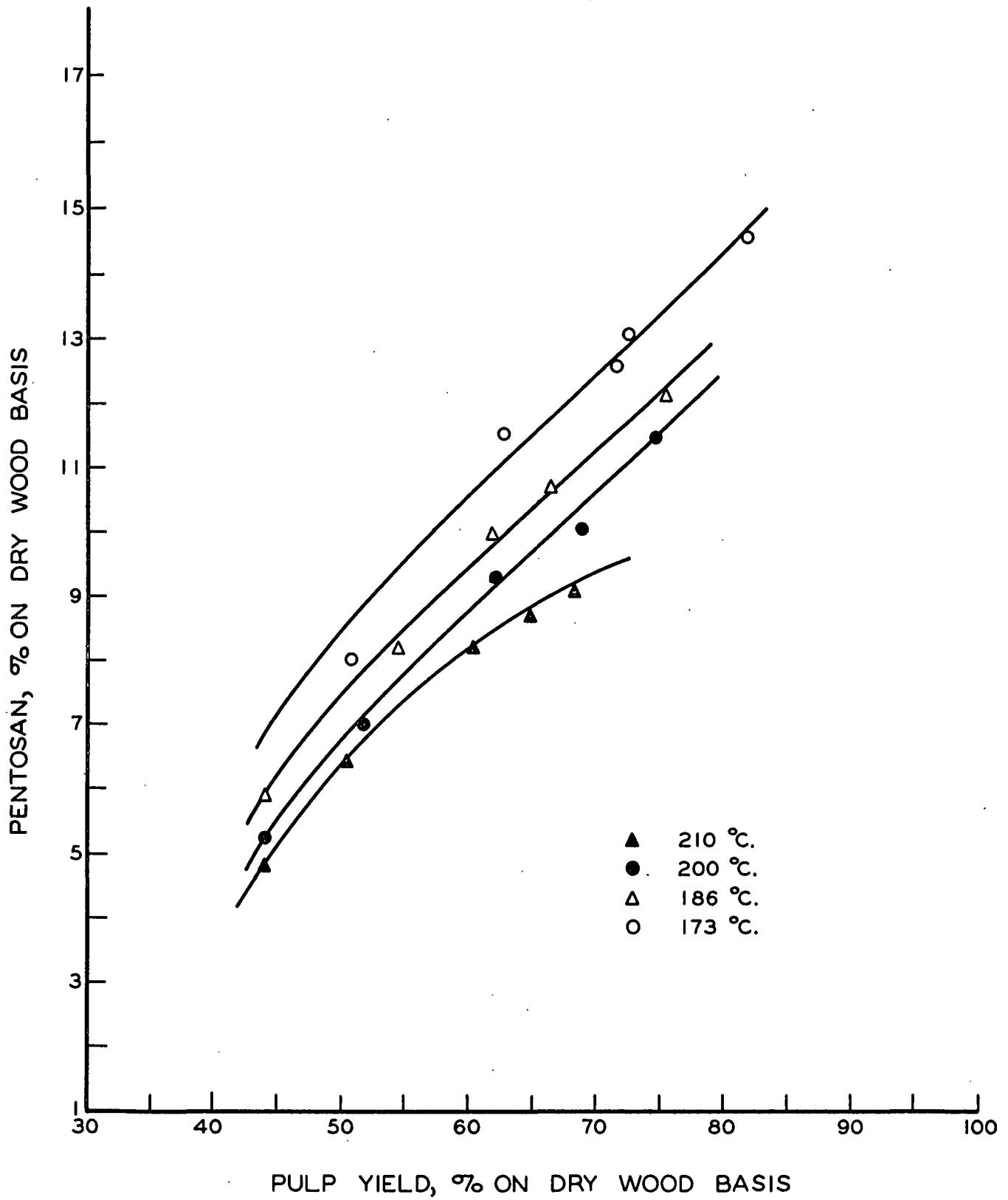


Figure 18. Pentosan Content vs. Pulp Yield

the pentosan data were plotted as a function of yield (Figure 18), the following could be observed. Increasing temperature of pulping decreased the pentosan content when pulps were compared at equivalent yields. This decrease in pentosan content was considerable, and for the over-all temperature range studied, amounted to approximately one-third of the pentosan material remaining in the pulp.

CUPRIETHYLENEDIAMINE VISCOSITY

To obtain an indication of the degree of polymerization (DP), the viscosity of a 0.5% solution of holocellulose in cupriethylenediamine was determined.¹ The results obtained can be found in Table V. When plotted against yield (Figure 19), the following relationships were observed. The viscosity of the holocellulose fraction decreased with increasing pulping temperature. The viscosity of a 210°C holocellulose was roughly half that of 173°C. holocellulose at comparable yields.

It should be noted that at the very high yields (above approximately 70%), there appears to be an increase in holocellulose viscosity with continued pulping. This is what would be expected, as, during the very early stages of pulping, the low molecular weight material originally present in the wood was probably being removed very rapidly. Also, during this period, the rate of degradation was probably not appreciable; hence, holocellulose viscosity should increase with continued pulping. At some point in the pulping cycle the effect of degradation would overshadow the removal of low molecular weight material originally present in the wood,

¹ Appendix, page 120

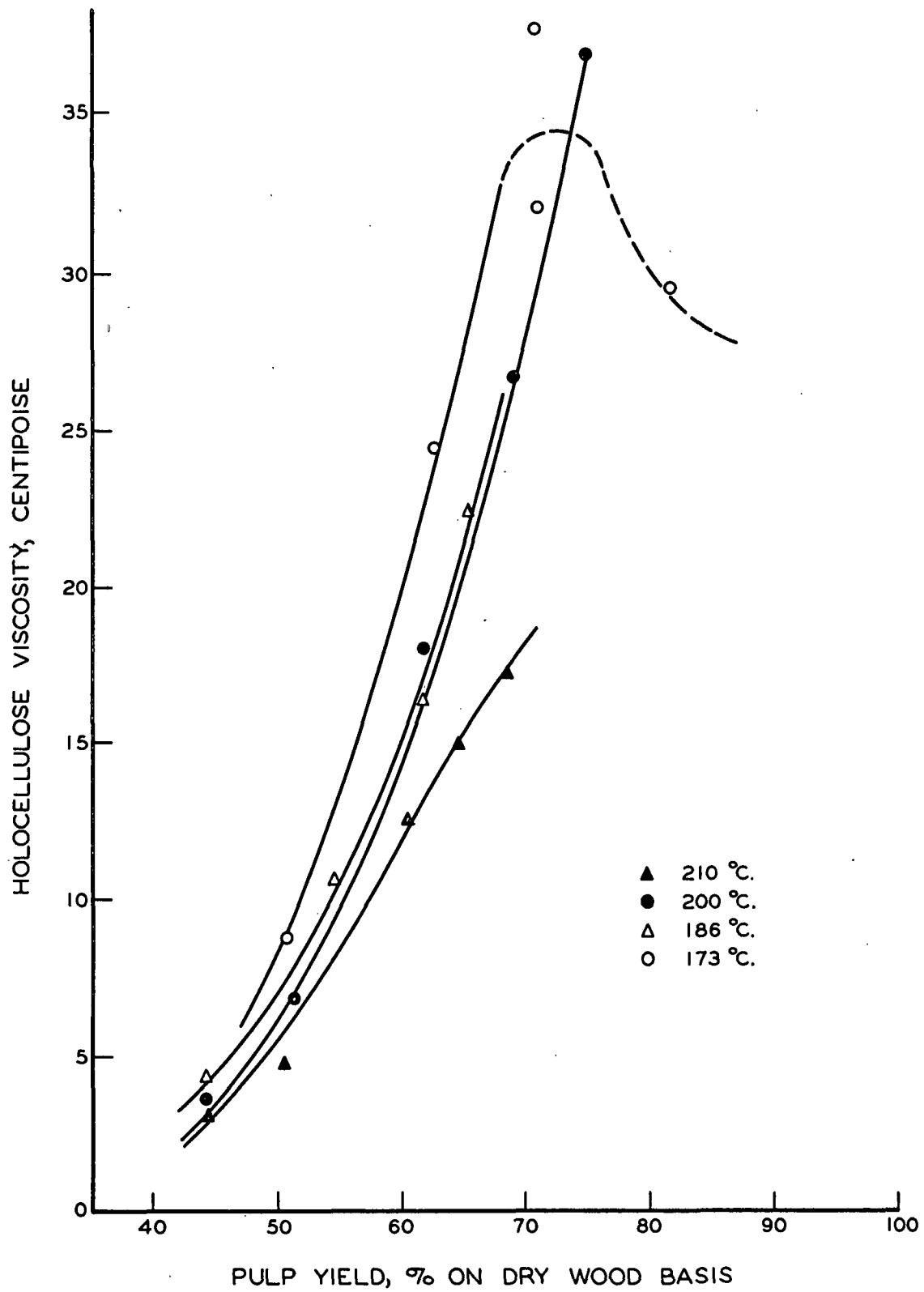


Figure 19. Holocellulose Viscosity vs. Pulp Yield

and, hence, with continued pulping, viscosity should decrease. It is felt that it was this effect which was observed in the viscosity measurements of the 173°C. isotherm but insufficient measurements were made in the high-yield range to plot accurately the path of the viscosity change.

The degradation of the long chain molecules alone could be studied by obtaining viscosity measurements of the alkali-resistant pulps. Samples of 21.5% alkali-resistant material were prepared, air dried, and treated with cupriethylenediamine. It was found experimentally, that these samples were only partially soluble in cupriethylenediamine and the values obtained were unreliable.

BRIGHTNESS

Pulp brightness was determined on aged pulps (56 to 58 hours) according to standard procedures¹, and the values obtained can be found in Table VI. Even though these values are exceptionally high, none of the pulps had been bleached.

The very bright pulps are probably a result of a combination of factors. The selective pulping of sapwood, limiting the chemical composition of the cooking liquor to pure sodium sulfite, and the use of stainless steel equipment throughout, all undoubtedly contribute to the brightness level. Furthermore, by cooking only at maximum temperature, the over-all pulping time was reduced considerably, even at conventional cooking temperatures. This abbreviated pulping time possibly contributed to increased brightness.

¹ Appendix, page 115

TABLE VI

BRIGHTNESS DATA

Cook No.	Temp. of Pulping, °C.	Yield, % ^a	GE Brightness, %
32	173°	81.7	58.2
31	173°	72.3	59.3
29	173°	71.3	58.6
39	173°	62.7	62.8
33	173°	50.8	74.1
34	186°	75.1	56.8
36	186°	66.1	60.0
35	186°	61.9	66.4
38A	186°	54.3	69.7
37	186°	44.0	75.4
40	200°	74.5	57.2
42	200°	68.9	57.8
43	200°	61.8	62.9
44	200°	51.7	71.9
41	200°	44.1	75.0
47	210°	68.2	54.8
46	210°	64.6	60.5
49	210°	60.1	63.5
48	210°	50.3	70.0
45	210°	43.9	73.9

^a Per cent yield based on oven-dry wood.

Before discussing the brightness values further, it is advisable to discuss certain color reactions which were observed during the experimental pulping and washing cycles. All of the pulps, upon removal from the digester, were considerably brighter than their measured values indicate. Immediately after pulping, the pulp color ranged between a very pale green-yellow to a bright white, and this color was stable so long as the pulp slurry contained a small portion of spent liquor. As the pulps were washed with fresh cold tap water, the pulps began to assume a red color. This red coloring matter was not soluble in cold water, as the wash water appeared to contain no unusual colored materials. Depending upon the temperature of cooking and the degree of pulping, the intensity of the red color in the pulp varied from a light pink to a brilliant red. Upon standing, the red color slowly disappeared, leaving the pulp more yellow than it was before reversion.

It was noticed that the reactions leading to the appearance and disappearance of the red coloring were light-sensitive, and storage of the pulp in a cool dark place delayed the reactions for as long as two weeks. If only small amounts of chlorine were present in the wash water, the red color would develop more rapidly and more intensely. Furthermore, the red coloring matter was readily soluble in ethyl alcohol, as it was always completely removed by extraction. The yield at which the most intense red color developed appeared to increase with pulping temperature. For example, at 173°C., the most brilliant red appeared at the lowest yield (50%). As the temperature of pulping increased, the point of highest color intensity moved to a yield of 60-65%.

The cooking liquor also displayed some unusual color reactions. At the lower pulping temperatures, the spent liquor was a reddish-brown. As the temperature of pulping increased, the spent liquor color changed to a yellowish-green. It is felt that considerable work still remains to be done in this area of color reactions for pulps and spent liquors produced from high-temperature cooks. However, such work was outside the scope of this thesis.

Brightness was plotted as a function of yield and temperature (Figure 20), and it can be seen that there was apparently no good correlation between the variables. This was probably the result of the variations in color reactions previously noted. Despite the lack of good relationships, certain broad trends are shown by the data. As would be expected, decreasing yield resulted in increased brightness for all pulping temperatures. Furthermore, throughout the entire yield range brightness appears to suffer slightly by cooking at elevated temperatures, but such brightness loss for the temperature range studied was probably not more than 3% as measured by the General Electric Brightness Meter.

INTRODUCTION TO THE PHYSICAL EVALUATION OF SHEET PROPERTIES

The physical properties obtainable in a sheet of paper produced from any given pulp represent a very important consideration in the evaluation of that pulp. The physical strengths alone, however, are not the only criteria for a successful evaluation from the papermaker's viewpoint. Instead, the papermaker must consider the interrelationships of physical properties in three distinct areas, namely: the power required

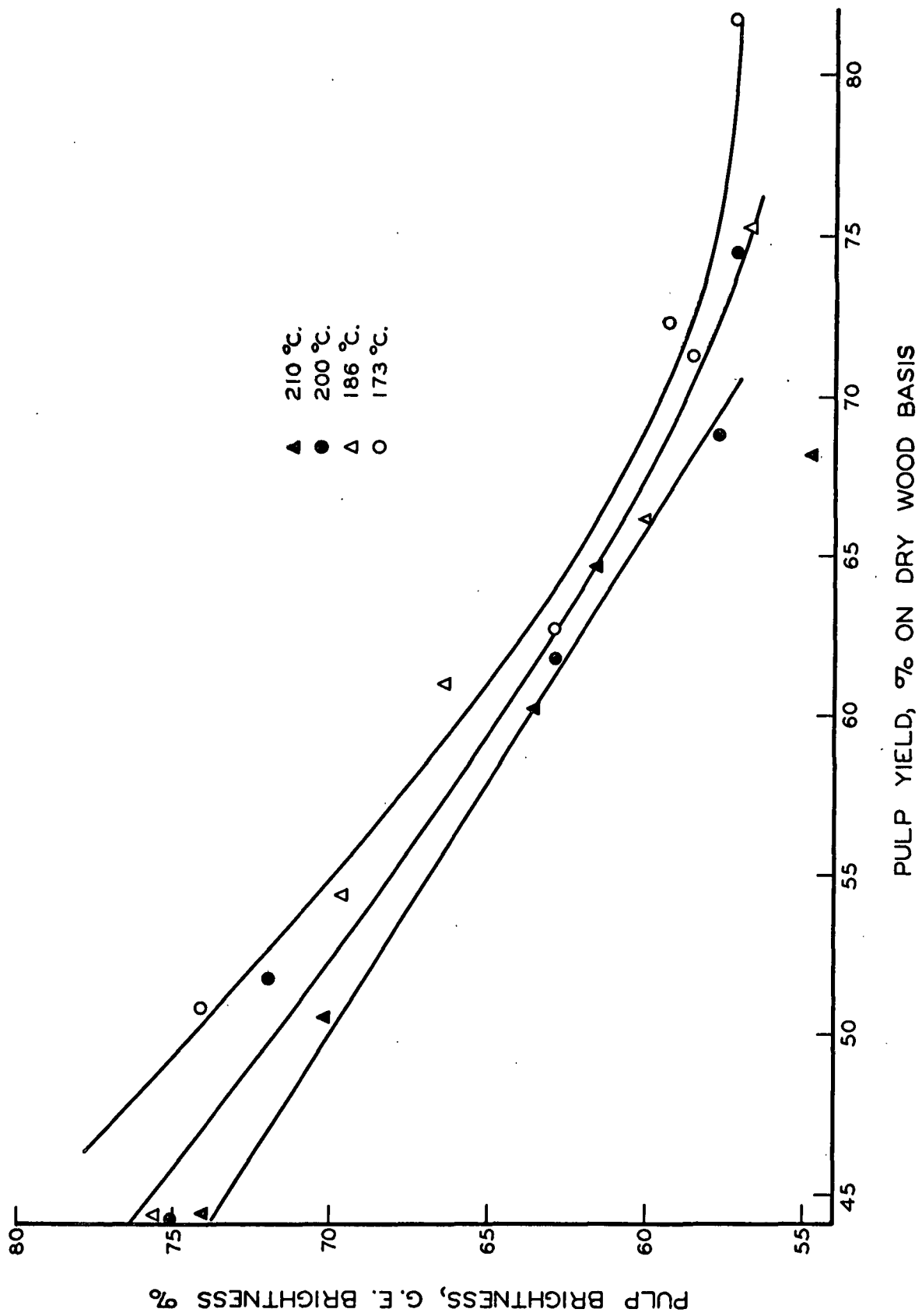


Figure 20. Pulp Brightness vs. Pulp Yield

for beating, the resulting drainage properties, and the physical characteristics of the finished paper. It is the complexity of these interrelationships which causes considerable difficulty in relating physical properties to cooking conditions.

Over-all strength values cannot be compared directly, as they are a function of beating. In certain ranges tear resistance, compressibility, flexibility, and opacity generally decrease, while tensile strength, bursting strength, folding endurance, abrasion resistance, and density increase with beating (25-29). These inverse relationships can be explained by realizing that the measured physical properties are dependent upon certain fundamental pulp qualities. The fiber strength, the amount and kind of fiber-to-fiber bonding, and the quantity and condition of the fibers present are the more fundamental properties which can be used in explaining the relationships of sheet strength and beating.

It is conceivable that the handsheet properties and beating characteristics of two pulps could be identical, with the pulp drainage characteristics being entirely different. During beating, pulp fibers swell, fibrillate, and are broken; the type and amount of these changes greatly affects sheet and drainage characteristics (30, 31). Drainage rates are important, as they help determine production limitations for the papermaker. Thus, it can be seen that any study of physical properties must, for completeness, be considered from the basis of all three fundamental variables: power requirements, drainage characteristics, and sheet properties.

In this work, the power requirements for beating will be considered to be directly related to beating time. Such a relationship involves two important assumptions. The first assumption is that the work done by the Sprout-Waldron refiner in fiberizing was constant for all the pulps, irrespective of yield. Obviously, such an assumption is not entirely correct, since the physical state of the pulp before fiberizing varied from a softened chip to a completely defibered pulp, depending upon pulp yield. Hence, different amounts of energy were probably absorbed during the fiberizing stage, and, in addition, the fiberizing cycle was conducted under conditions not conducive to equal energy input. The second assumption is that the power input per unit time of beating and the action imparted by the beater were constant. Because of the experimental techniques employed and the great similarity between the pulps as is evident from a study of both chemical and physical properties, power expenditure and beating time are probably closely related. Hence, in the remainder of this thesis, beating time will be considered a direct measure of the energy expended in beating the pulp.

Additional difficulty arose in the interpretation of the measurements of the drainage characteristics of the pulps studied. Routine control methods such as Canadian standard freeness and Schopper-Riegler freeness do not measure the essential pulp drainage properties necessary for a fundamental study (31, 32). Better evaluation of fundamental drainage properties could be obtained by the measurement of filtration resistance, but the time required rendered this impractical, owing to the number of pulps and beating intervals that were investigated. Therefore, in this

thesis, the Schopper-Riegler freeness test was used as a measure of drainage characteristics, despite its serious limitations.

When studying pulps of widely varying yield values, another factor must be considered. Paper is generally sold on the basis of a specific weight, and, therefore, the papermaker is most interested in physical properties based on constant weight per unit area. For a theoretical understanding, it is often desirable to compare physical properties of sheets containing equivalent cellulosic material. In this work, all the sheet properties were measured on the basis of a constant sheet weight, and, where possible, a mathematical correction to constant cellulosic weight was made. This correction will be discussed subsequently as it is used.

DENSITY

Basis weight and caliper are the measured variables which determine apparent sheet density, and, therefore, it is appropriate to consider these three properties simultaneously. The values of basis weight, caliper, and density can be found in Table VII. A study of sheet weight revealed that out of the hundred sets of handsheets made, only fourteen differed from the mean weight (65.5 g. per sq. m.) by greater than 2%. In considering these fourteen sets, only two sets had a weight variation from the mean greater than 3%. The weight variation between sets, therefore, was well within the $\pm 5\%$ limits set up by TAPPI Standards (33). This limited weight variation was quite significant when considering methods of adjusting the measured physical properties for weight variation.

TABLE VII

PHYSICAL EVALUATION OF PULPS PRODUCED AT 173°C.

Cook No. and Yield, %	Beating Time, min.	Basis Weight, g./sq. m.	Caliper, mils	Apparent Density, g./cc.	Tensile Strength, lb./in. ²	Corrected Tensile, lb./in. ²	Elmendorf Tear Factor ^c	Corrected Elmendorf Tear ^c	Clark Rigidity Factor	Stretch, %	Schopper- Reigler Freeness, cc.	B & L Opacity, %
Cook 32	5	65.95	4.0	0.65	22.9	28.3	77.3	95.5	89.3	2.00	830	72.0
Yield	10	66.08	3.6	0.72	27.3	33.7	69.6	86.0	110.3	2.60	800	70.5
81.7%	20	65.67	3.2	0.81	31.7	39.1	64.0	79.1	146.3	2.97	670	68.0
	30	67.32	3.1	0.85	35.7	44.1	55.0	67.9	144.9	3.57	460	63.5
	40	65.35	3.0	0.86	36.9	45.6	56.6	69.9	145.9	3.57	405	62.5
Cook 31	5	64.67	3.5	0.73	34.4	39.6	74.2	85.3	131.1	3.13	850	72.0
Yield	10	65.43	3.2	0.80	37.5	43.1	68.8	79.1	161.7	3.40	830	68.5
72.3%	20	65.77	3.0	0.86	42.3	48.6	63.9	73.4	171.2	4.07	720	62.5
	30	64.51	2.9	0.88	43.1	49.5	58.9	67.7	159.0	4.07	510	56.5
	40	65.40	2.8	0.92	46.0	52.9	56.6	65.0	180.8	4.33	410	53.5
Cook 29	5	66.17	3.6	0.72	32.4	37.6	78.6	91.3	138.3	2.67	855	73.0
Yield	10	65.71	3.2	0.81	40.1	46.6	67.0	77.9	171.6	3.67	815	69.0
71.3%	20	66.20	3.1	0.84	41.4	48.1	66.5	77.3	173.6	3.53	675	64.0
	30	65.55	2.9	0.89	41.0	47.7	54.9	63.8	154.3	4.07	545	56.5
	38	67.14	3.0	0.88	43.2	50.3	56.6	65.7	158.4	4.27	395	49.5
Cook 39	5	65.92	3.4	0.76	39.5	43.3	72.8	79.7	164.4	3.40	830	73.5
Yield	10	65.61	3.2	0.81	44.3	48.5	70.1	76.8	163.0	3.87	810	69.0
62.7%	20	66.30	3.1	0.84	45.8	50.1	64.9	71.1	171.8	4.03	720	64.5
	30	65.76	3.0	0.86	47.4	51.9	60.8	66.6	166.1	4.27	525	59.5
	40	65.43	2.9	0.89	44.4	48.6	65.7	71.9	177.0	3.73	465	58.5
Cook 33	5	64.81	3.3	0.77	34.7	35.9	83.3	86.4	174.7	3.03	780	74.5
Yield	10	65.55	3.2	0.81	36.4	37.8	82.4	85.4	171.8	3.37	750	71.5
50.8%	20	65.30	3.1	0.83	40.1	41.5	82.7	85.7	175.4	3.83	650	68.5
	30	64.19	2.9	0.87	42.0	43.6	70.1	72.7	184.0	4.17	515	64.5
	40	65.09	2.9	0.88	40.3	41.8	75.3	78.1	182.0	4.00	445	64.0

^a Tensile strength expressed in terms of pounds per inch at a sheet weight of 65.5 g. per sq. m.

^b Corrected tensile expressed in terms of pounds per inch at a sheet weight of cellulose material equal to 65.5 g. per sq. m.

^c Tear factor expressed in grams of force required to tear a sheet of 100 g. per sq. m. basis weight.

^d Corrected tear expressed in grams of force required to tear a sheet of 110 g. per sq. m. cellulosic weight.

^e Stretch expressed as percentage elongation of specimen at rupture under tensile strain.

^f B & L Opacity = opacity by contrast ratio—100 R₀/R_{0.89}

TABLE VII (continued)

PHYSICAL EVALUATION OF PULPS PRODUCED AT 186°C.

Cook No. and Yield, %	Beating Time, min.	Basis Weight, g./sq. m.	Caliper, mils	Apparent Density, g./cc.	Tensile Strength, lb./in. ²	Corrected Tensile, lb./in. ²	Elmendorf Tear Factor ^c	Corrected Elmendorf Tear ^d	Clark Rigidity Factor	Stretch, %	Schopper- Riegler Freeness, cc.	B & L Opacity, %
Cook 34	5	65.14	3.8	0.67	24.6	29.8	82.9	100.4	98.2	2.33	830	74.0
Yield	10	65.52	3.5	0.74	29.3	35.5	74.8	90.6	129.7	2.73	800	72.5
75.1%	20	65.35	3.2	0.80	34.4	41.7	67.3	81.5	148.8	3.57	670	70.0
	30	65.78	3.1	0.84	37.2	45.1	65.4	79.2	159.0	2.18	585	65.5
	40	64.74	3.0	0.85	38.9	47.1	60.2	72.9	158.7	3.73	430	64.0
Cook 36	5	66.10	3.6	0.72	36.1	41.2	80.2	91.7	155.8	2.97	850	78.0
Yield	10	64.06	3.3	0.76	40.4	46.1	71.8	82.1	174.1	3.20	820	74.0
66.1%	20	65.14	3.2	0.80	39.9	45.5	69.1	79.0	166.4	3.37	745	70.0
	30	65.59	3.0	0.86	44.0	50.2	65.6	75.0	199.7	3.57	590	66.5
	40	65.09	2.8	0.92	44.6	50.9	55.3	63.2	190.1	4.13	345	59.5
Cook 35	5	65.33	3.4	0.76	35.6	39.1	78.1	85.8	165.2	3.10	835	74.0
Yield	10	65.02	3.2	0.80	40.6	44.6	72.3	79.4	169.8	3.50	790	69.5
61.9%	20	65.51	3.0	0.86	44.2	48.6	67.2	73.8	191.7	3.90	665	65.5
	30	64.85	2.9	0.88	44.4	48.8	63.2	69.4	178.4	4.03	480	62.0
	40	67.87	3.0	0.89	45.3	49.8	63.4	69.7	189.3	4.03	390	62.5
Cook 38A	5	65.15	3.4	0.75	36.1	37.9	92.1	96.6	167.4	3.23	780	77.0
Yield	10	64.55	3.2	0.79	38.4	40.3	85.2	89.4	177.7	3.33	755	74.5
54.3%	20	65.55	3.1	0.83	38.4	40.4	82.4	86.5	191.9	3.33	670	71.0
	30	65.30	3.0	0.86	42.4	44.5	75.0	78.7	194.0	3.90	865	69.0
	40	65.19	3.0	0.86	45.1	47.4	79.8	83.8	185.7	3.90	470	67.5
Cook 37	5	64.28	3.4	0.74	32.1	33.2	73.1	75.7	168.5	2.97	770	78.0
Yield	10	65.09	3.2	0.80	35.7	36.9	67.6	69.9	176.8	3.30	695	76.0
44.0%	20	65.17	3.0	0.86	38.5	39.9	59.8	61.9	221.0	3.40	520	72.5
	30	64.20	2.7	0.94	38.1	39.8	49.8	51.5	195.4	3.90	245	66.5
	40	66.13	2.6	1.00	35.9	37.1	42.3	43.8	188.1	3.97	130	59.5

^a Tensile strength expressed in terms of pounds per inch at a sheet weight of 65.5 g. per sq. m.

^b Corrected tensile expressed in terms of pounds per inch at a sheet weight of cellulose material equal to 65.5 g. per sq. m.

^c Tear factor expressed in grams of force required to tear a sheet of 100 g. per sq. m. basis weight.

^d Corrected tear expressed in grams of force required to tear a sheet of 110 g. per sq. m. cellulosic weight.

^e Stretch expressed as percentage elongation of specimen at rupture under tensile strain.

^f B & L Opacity = opacity by contrast ratio—100 R₀/R_{0.89}

TABLE VII (continued)

PHYSICAL EVALUATION OF PULPS PRODUCED AT 200°C.

Cook No. and Yield, %	Beating Time, min.	Basis Weight, g./sq. m.	Caliper, mils	Apparent Density, g./cc.	Tensile Strength, lb./in. ²	Corrected Tensile, lb./in. ²	Elmendorf Tear Factor ^c	Corrected Elmendorf Tear ^c	Clark Rigidity Factor	Stretch, %	Schopper- Riegler Freeness, cc.	B & L Opacity, %
Cook 40	5	65.01	3.8	0.67	25.1	30.5	78.4	95.2	108.2	2.20	835	76.0
	10	65.22	3.6	0.71	28.7	34.9	75.1	91.2	124.7	2.73	805	75.5
Yield	20	65.32	3.4	0.76	33.1	40.2	70.4	85.5	139.8	3.03	690	73.0
74.5%	30	67.85	3.4	0.79	35.7	43.4	66.3	80.5	137.8	3.33	565	73.5
	40	67.05	3.1	0.85	37.4	45.4	62.6	76.0	159.8	3.43	350	69.0
Cook 42	5	65.75	3.6	0.72	33.2	38.8	80.6	94.2	136.5	2.80	840	76.0
	10	66.11	3.4	0.77	38.1	44.5	75.6	88.3	159.0	3.17	800	75.0
Yield	20	65.66	3.2	0.81	38.7	45.2	71.6	83.6	162.7	3.23	740	71.0
68.9%	30	65.72	3.0	0.86	39.7	46.4	63.9	74.7	163.8	3.43	490	67.5
	40	64.43	2.9	0.87	40.8	47.7	63.6	74.3	165.1	3.77	310	62.0
Cook 43	5	65.84	3.5	0.74	36.8	41.2	82.0	91.8	161.3	3.00	830	75.0
	10	65.60	3.3	0.78	38.7	43.4	76.2	85.4	147.3	3.20	810	73.5
Yield	20	65.06	3.1	0.83	40.8	45.7	73.8	82.6	174.3	3.33	670	68.5
61.8%	30	65.84	3.1	0.84	41.9	46.9	72.9	81.6	171.5	3.63	610	68.0
	40	65.09	3.0	0.85	44.5	49.8	67.6	75.7	170.2	3.77	415	64.5
Cook 44	5	63.63	3.5	0.72	30.9	32.3	88.0	92.0	149.9	2.63	790	79.0
	10	63.87	3.3	0.76	34.7	36.3	87.7	91.7	166.0	2.93	740	76.0
Yield	20	64.31	3.2	0.79	37.5	39.2	80.6	84.3	170.7	3.50	660	73.5
51.7%	30	65.08	3.2	0.80	38.0	39.7	75.3	78.8	171.2	3.43	555	72.5
	40	64.23	3.0	0.84	40.4	42.2	70.1	73.3	185.3	3.67	420	70.5
Cook 41	5	65.70	3.5	0.74	25.8	26.5	71.5	73.6	170.0	3.00	760	78.0
	10	64.45	3.2	0.79	33.0	33.9	69.8	71.8	188.0	3.13	715	76.0
Yield	20	63.57	3.0	0.83	35.2	36.3	58.2	60.0	196.4	3.20	535	72.5
44.1%	30	64.70	2.9	0.88	35.2	36.3	54.1	55.7	190.2	3.27	320	70.0
	40	64.87	2.7	0.95	39.5	40.7	46.2	47.6	195.5	—	170	64.0

^a Tensile strength expressed in terms of pounds per inch at a sheet weight of 65.5 g. per sq. m.

^b Corrected tensile expressed in terms of pounds per inch at a sheet weight of callulosic material equal to 65.5 g. per sq. m.

^c Tear factor expressed in grams of force required to tear a sheet of 100 g. per sq. m. basis weight.

^d Corrected tear expressed in grams of force required to tear a sheet of 110 g. per sq. m. callulosic weight.

^e Stretch expressed as percentage elongation of specimen at rupture under tensile strain.

^f B & L Opacity = opacity by contrast ratio $R_0/R_{0.89}$

TABLE VII (continued)
PHYSICAL EVALUATION OF PULPS PRODUCED AT 210°C.

Cook No. and Yield, %	Beating Time, min.	Basis Weight, g./sq. m.	Caliper, mils	Apparent Density, g./cc.	Tensile Strength, lb./in. ²	Corrected Tensile, lb./in. ²	Elmendorf Tear Factor ^c	Corrected Elmendorf Tear	Clark Rigidity Factor	Stretch, %	Schopper- Riegler Freeness, cc.	B & L Opacity, %
Cook 47	5	64.29	3.5	0.72	31.8	37.2	82.4	96.4	148.2	2.60	800	80.0
Yield	10	66.19	3.4	0.77	33.3	39.0	78.6	92.0	156.0	2.83	775	77.5
68.2%	20	63.74	3.2	0.78	37.3	43.6	73.7	86.3	159.3	3.23	675	75.5
	30	63.70	3.0	0.84	39.4	46.1	70.6	82.6	173.4	3.40	530	74.5
	40	63.87	2.9	0.87	40.5	47.4	65.8	77.0	182.5	3.40	370	71.5
Cook 46	5	65.16	3.6	0.71	31.5	35.5	85.9	96.7	145.2	2.67	830	77.5
Yield	10	64.29	3.4	0.74	36.8	41.5	82.4	92.8	154.6	3.23	810	75.0
64.6%	20	64.71	3.2	0.80	38.2	43.0	78.8	88.7	164.7	3.50	705	72.0
	30	64.41	3.1	0.82	40.6	45.7	71.4	80.3	162.4	3.90	545	69.5
	40	65.18	3.0	0.86	40.0	45.1	69.0	77.7	182.3	3.70	455	70.5
Cook 49	5	64.92	3.5	0.73	32.4	36.0	89.3	99.1	160.5	2.57	820	78.5
Yield	10	66.04	3.4	0.76	37.5	41.6	83.3	92.5	178.1	3.20	790	76.5
60.1%	20	64.79	3.2	0.80	40.4	44.8	75.6	83.9	178.3	3.33	700	73.0
	30	64.60	3.0	0.85	41.0	45.5	71.2	79.0	183.5	3.47	555	70.0
	40	64.65	3.0	0.85	41.2	45.7	68.1	75.5	175.3	3.63	475	70.5
Cook 48	5	65.01	3.6	0.71	31.4	34.2	86.1	90.9	163.0	2.63	760	80.5
Yield	10	65.47	3.4	0.76	33.1	35.0	82.5	87.1	183.2	2.83	720	78.5
50.3%	20	64.43	3.2	0.79	36.9	39.0	72.9	87.1	179.5	3.26	615	75.0
	30	64.73	3.0	0.85	37.4	39.5	74.1	78.2	208.0	3.14	455	73.5
	40	64.44	2.8	0.91	38.9	41.1	59.0	62.4	185.8	3.80	275	70.0
Cook 45	5	64.55	3.6	0.71	32.0	33.3	68.2	70.9	150.8	2.97	725	80.5
Yield	10	64.95	3.3	0.77	34.7	36.0	61.6	64.1	168.2	3.17	645	78.5
43.9%	20	64.21	3.1	0.82	35.9	37.3	57.6	59.9	169.8	3.47	410	72.0
	30	64.41	2.8	0.91	35.0	36.4	48.1	50.0	178.7	3.78	170	72.5
	40	64.84	2.6	0.98	32.1	33.4	40.1	41.6	173.0	3.56	110	67.0

a Tensile strength expressed in terms of pounds per inch at a sheet weight of 65.5 g. per sq. m.
b Corrected tensile expressed in terms of pounds per inch at a sheet weight of cellulosic material equal to 65.5 g. per sq. m.
c Tear factor expressed in grams of force required to tear a sheet of 100 g. per sq. m. basis weight.
d Corrected tear expressed in grams of force required to tear a sheet of 110 g. per sq. m. cellulosic weight.
e Stretch expressed as percentage elongation of specimen at rupture under tensile strain.
f B & L Opacity = opacity by contrast ratio— $R_0/R_{0.89}$

Density was calculated in terms of grams per cubic centimeter, and the values obtained were plotted as a function of beating time. An example of such a plot may be found in the Appendix (Figure 44). To make comparisons at constant yield values, the apparent densities at constant beating time were determined using the plots of density versus beating time mentioned above. This information was then replotted as a function of yield. Examples of the plots obtained may be found in Figures 21 and 22. These data relating apparent sheet density and pulp yield at constant beating showed considerable scatter at any given beating time. However, less scatter existed in the data representing the initial stages of beating. At these initial beating intervals the data indicate that increasing pulping temperature produced bulkier sheets. As beating progressed, the data obtained showed trends only, with the temperature effect being approximately the same.

TEARING RESISTANCE

Tearing resistance was determined according to standard procedures¹, and a tear factor expressed in terms of grams of force per 100 grams per square meter of airdry basis weight was calculated. The use of the tear factor term in measuring tear resistance automatically corrects for weight variation between sheets.

The tear factor values can be found tabulated in Table VII. To make comparisons at constant yield values, the tear factors at constant beating intervals were measured from plots of tear versus beating. Graphs of tear

¹ Appendix, page 121

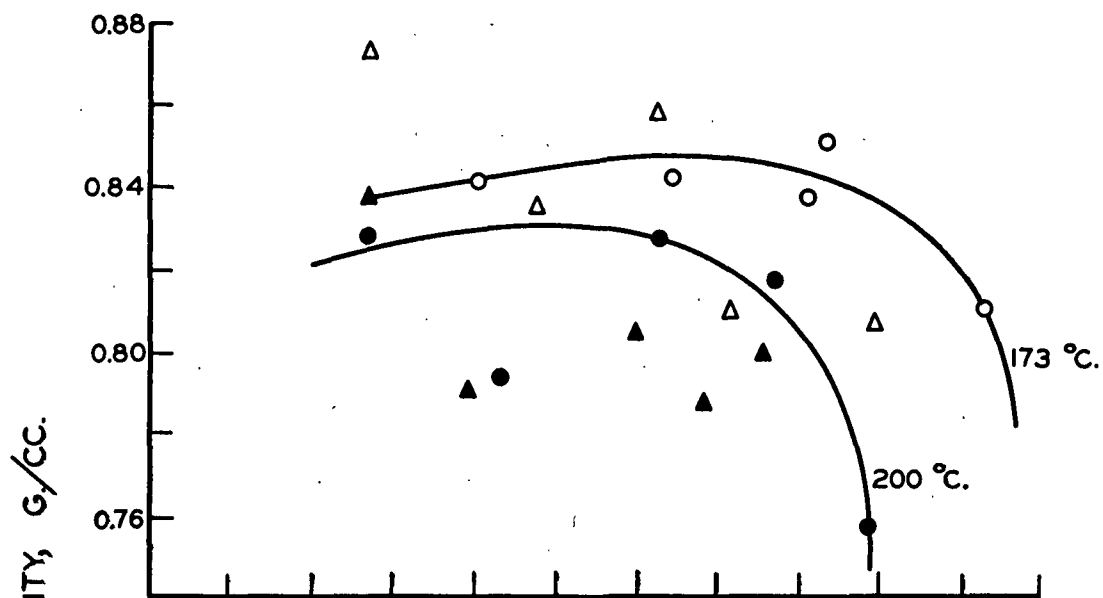


Figure 21. Sheet Density vs. Pulp Yield
(20-min. Beating Time)

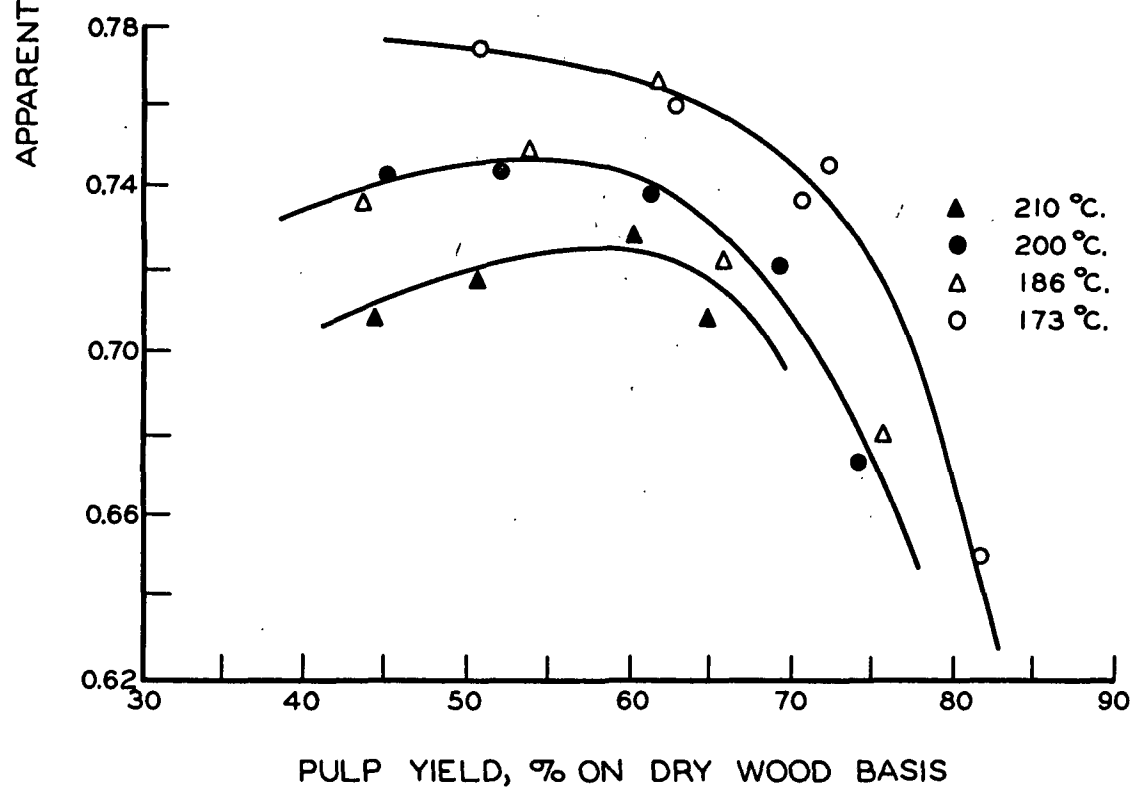


Figure 22. Sheet Density vs. Pulp Yield
(5-min. Beating Time)

factor versus yield at constant beating time were made (Figures 23 and 24), and these plots revealed some interesting information relating tear factor, yield, beating time, and temperature of pulping. In the high-yield range (approximately 50% and above), increasing pulping temperature increased the tear factor. At lower yields, temperature of pulping appeared to have little, if any, effect on tear.

Plots of tear factor versus apparent sheet density were made, and can be found in the Appendix (Figures 47 and 48). Using the techniques previously described, plots of tear factor versus yield at constant density were made (Figure 25). As might be expected, tear factor decreased with increasing density, and comparisons at constant density yielded similar results as obtained in comparisons at constant beating time.

In the previous paragraphs, the tear factor considered was based on constant sheet weight. In an attempt to compensate for the substantial differences in lignin content at the various yield levels, the constant weight data was corrected to a "corrected tear factor" based on constant carbohydrate weight of 65.5 grams carbohydrate material per square meter by assuming that the tear factor was directly proportionate to the weight of carbohydrate material.

$$\text{corrected tear} = \frac{\text{measured tear} \times 65.5}{\text{sheet weight} \times \% \text{ holocellulose}}$$

The corrected tear data was analyzed with respect to beating time and density by procedures used previously in the evaluation of tear

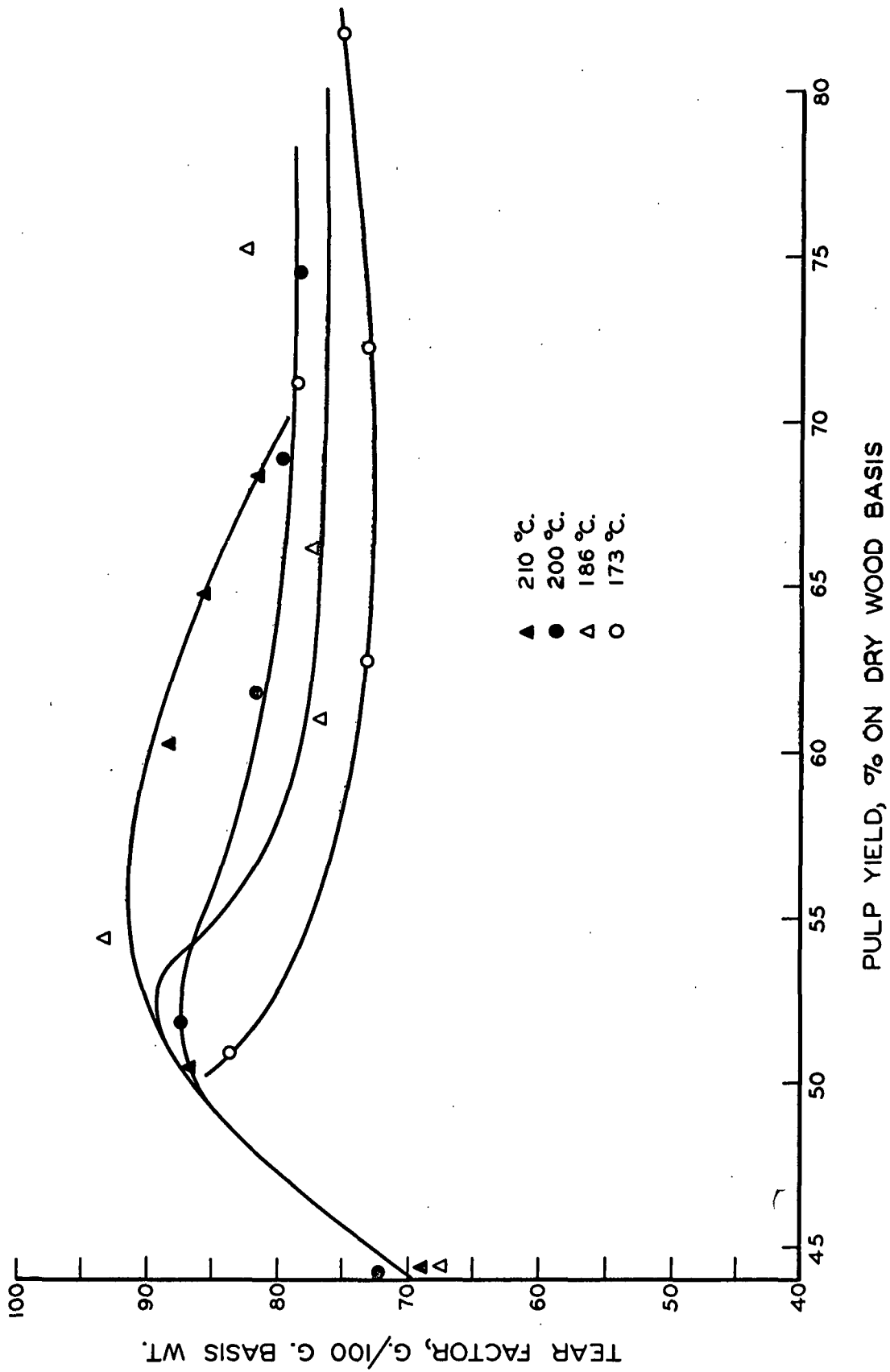


Figure 23. Tear Factor vs. Pulp Yield (5-Min. Beating Time)

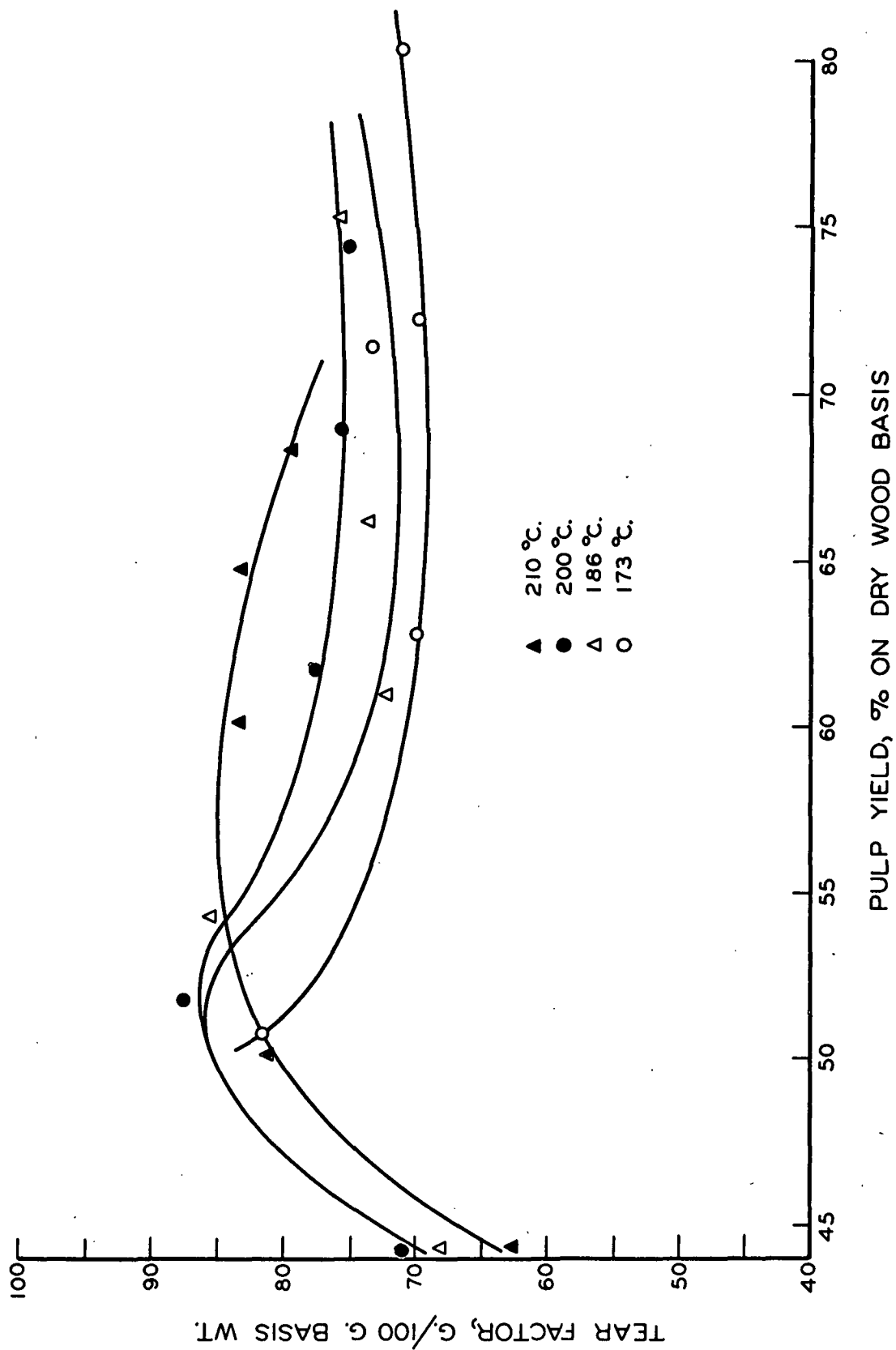


Figure 24. Tear Factor vs. Pulp Yield (10-Min. Beating Time)

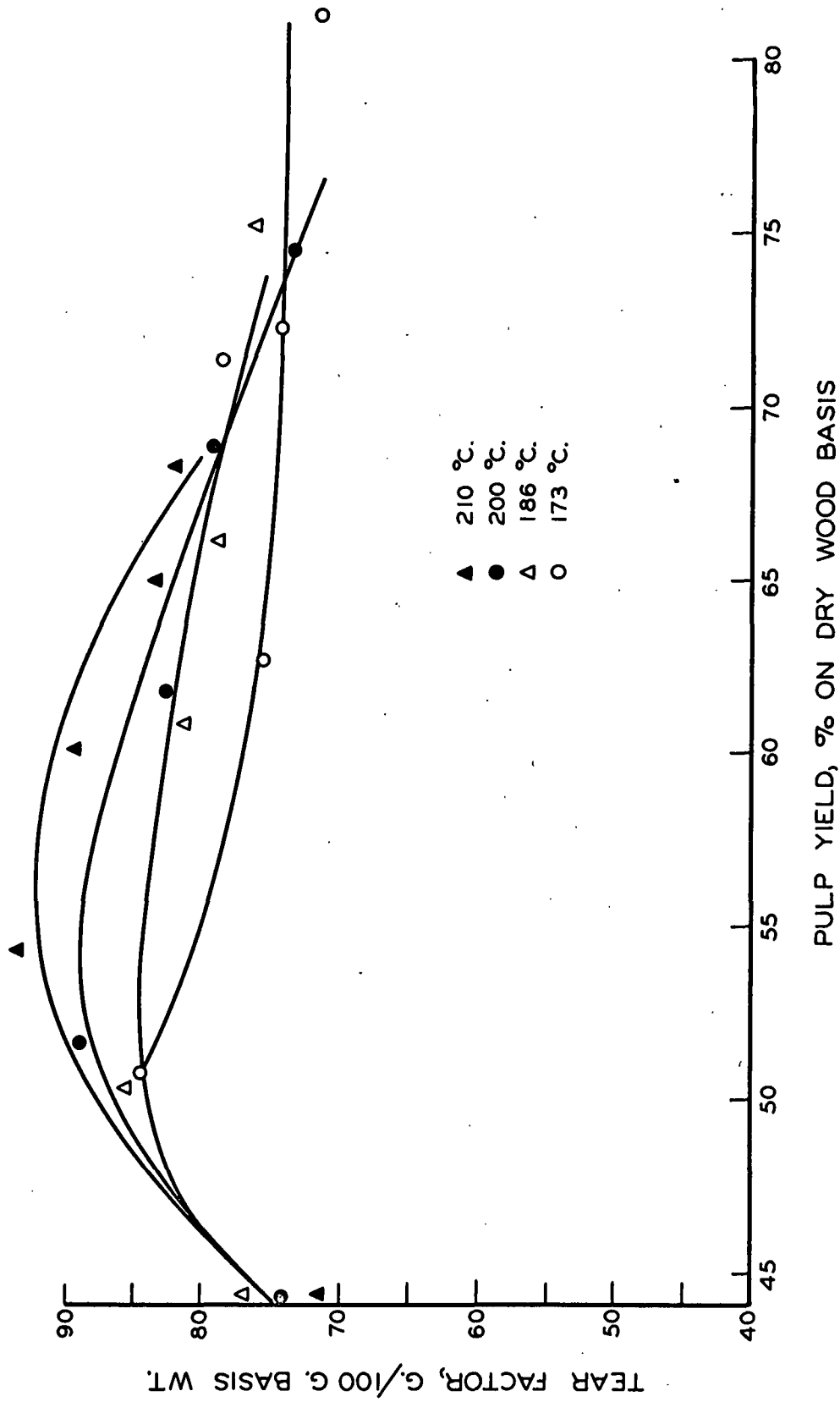


Figure 25. Tear Factor vs. Pulp Yield (.73 Sheet Density)

factor. Again, relationships similar to those obtained for the normal tear value were observed. Thus, in this case, correcting to constant carbohydrate was unnecessary. The only difference between the two methods appeared to be in the order of magnitude of the respective values. Sufficient plots to show the similarity between methods are enclosed in the appendix (Figures 49, 50, and 51).

TENSILE STRENGTH

Tensile strength was determined according to standard procedures¹, and the observed results reported in terms of lbs. per inch. These measured values were corrected for sheet weight variation by assuming that tensile strength would vary in direct proportion to sheet weight.

$$\text{tensile} = \frac{\text{measured tensile} \times 65.5}{\text{sheet weight}}$$

Bauer (34) has shown that when the sheet weight variation is limited to less than $\pm 5\%$ of the mean, this assumption of a direct relationship between basis weight and tensile strength introduces no significant error.

The weight-corrected data (Table VII) was analyzed by the technique used throughout this thesis, that is, tensile strength was plotted as a function of beating time, and then additional comparisons of tensile strength at constant beating time versus yield were made. As expected, tensile strength increased with beating. The very low yield pulps usually showed a maximum at about 25 minutes of beating, while the high yield pulps continued to increase in tensile value throughout the

¹ Appendix, page 121

beating range studied. Examples of the tensile versus beating time plots can be found in the Appendix (Figures 52 and 53). Comparisons of tensile strength at constant beating time and equivalent yield showed that high-temperature pulps were slightly weaker (Figure 26 and 27).

As was the case with tearing resistance, it was thought advisable to compare tensile values on the basis of constant carbohydrate weight. Tensile strengths were mathematically corrected to this basis by assuming proportionality between tensile strength and carbohydrate content. The corrected values obtained were compared at constant beating time by means identical to those previously discussed. Figure 54 in the Appendix is an example of such a plot. It can be seen that the corrected tensile behaved identically to the measured tensile strength, and, hence, need not be discussed in detail.

STRETCH

Stretch and tensile strength were determined simultaneously on the same test specimen¹. The total elongation of the specimen at failure was expressed as a percentage of the test length, and termed "Stretch". A statistical study of the effect of basis weight on stretch values has shown that if the weight variation is less than 5% of the mean, the variation in stretch due to weight is almost insignificant (34). Therefore, no attempt was made to correct stretch for basis weight variations; the values obtained can be found tabulated in Table VII. As usual, stretch was plotted against beating time. The curves obtained are very similar

¹ Appendix, page 121

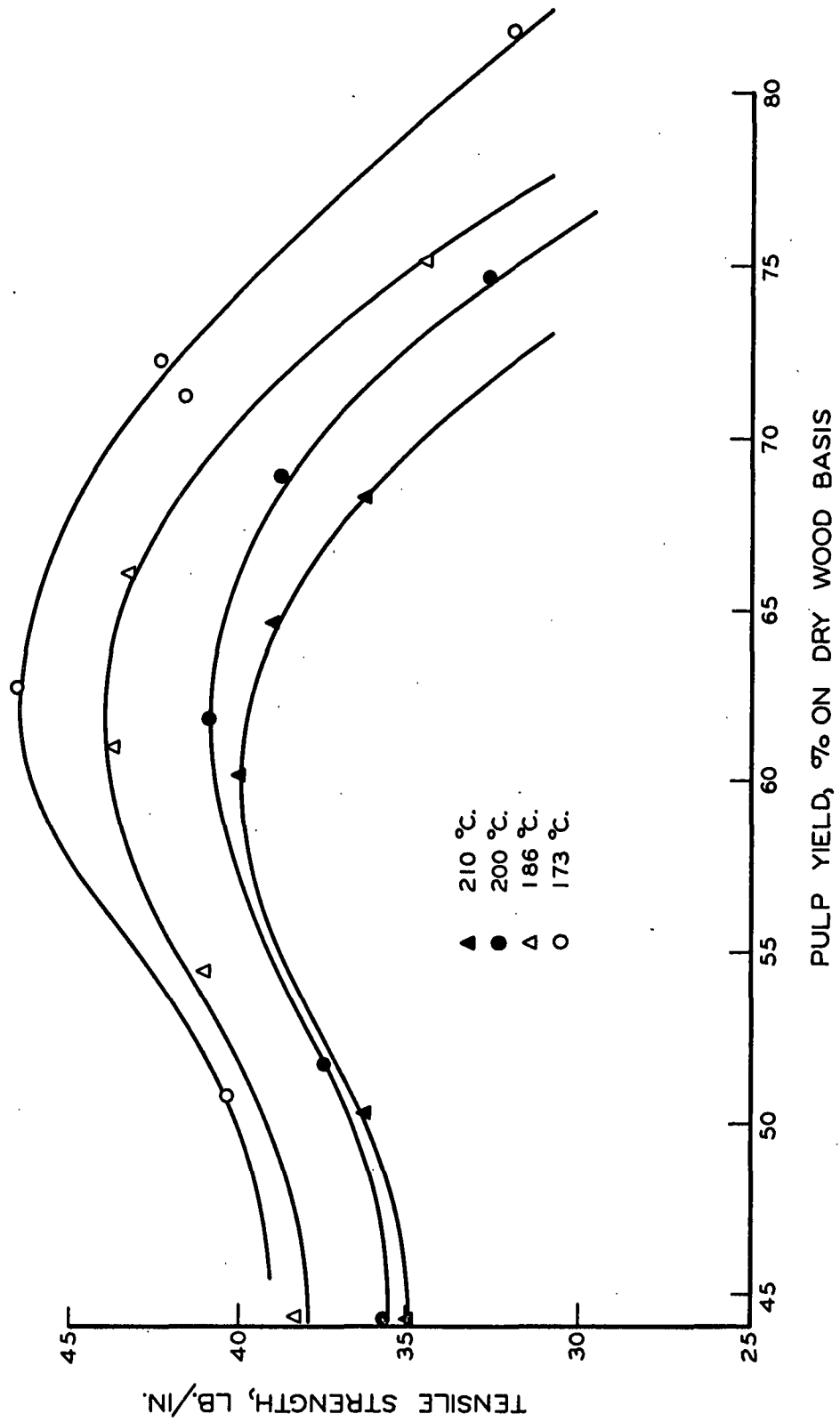


Figure 26. Tensile Strength vs. Pulp Yield (20-Min. Beating Time)

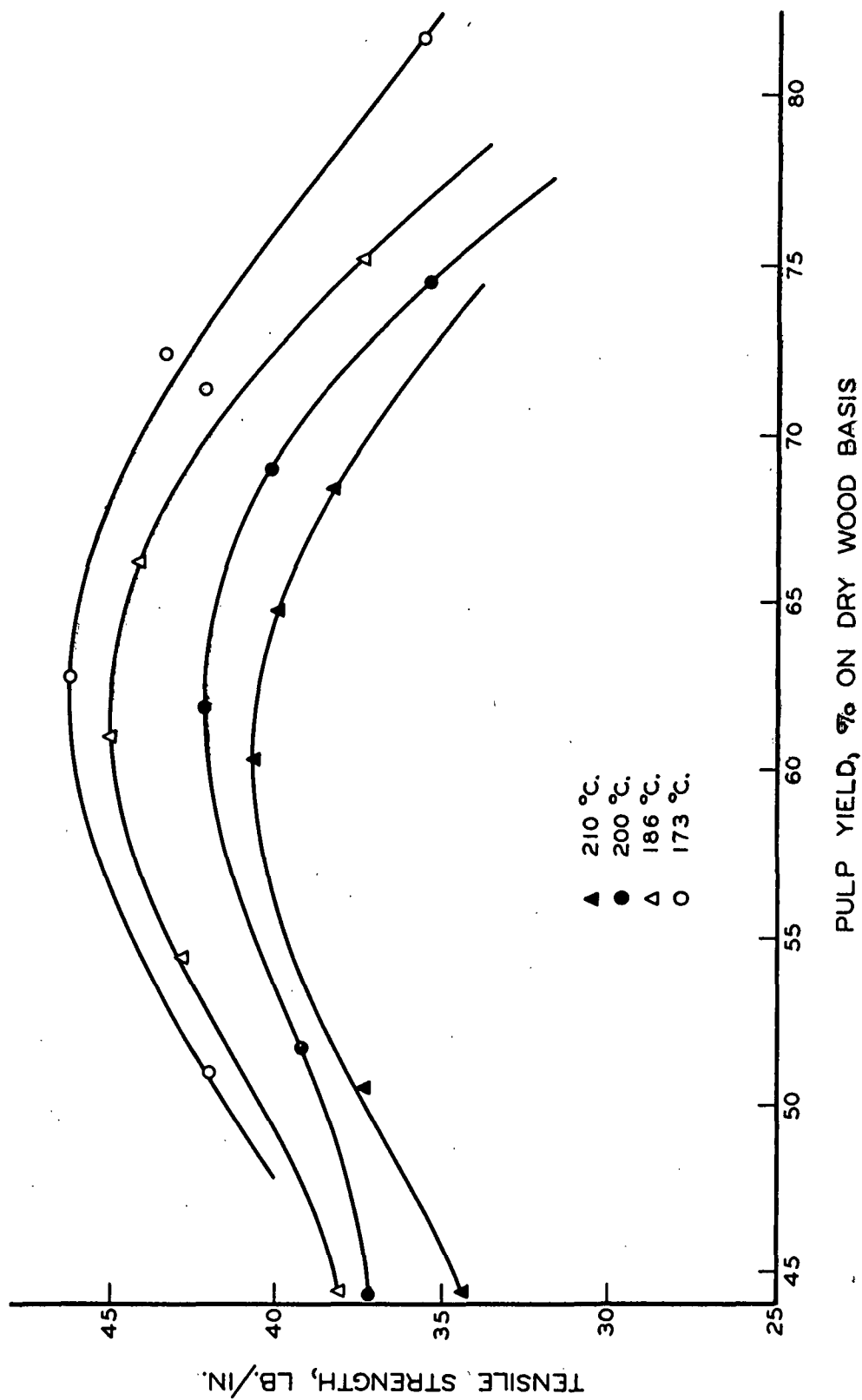


Figure 27. Tensile Strength vs. Pulp Yield (30-Min. Beating Time)

to those obtained for tensile strength, as the percentage stretch increased with increased beating. An example of a curve of stretch versus beating time can be found in the Appendix (Figure 46).

Stretch was plotted against yield at constant beating time, and examples of the curves obtained can be found in Figures 28 and 29. It can be seen that stretch decreased with increasing pulping temperature throughout the entire yield range investigated.

ZERO-SPAN TENSILE STRENGTH

The zero-span tensile strength was determined according to standard procedures¹, and the results obtained can be found tabulated in Table VIII. The measured value of zero-span strength was adjusted for basis weight variation by assuming a direct proportionality relationship.

$$\text{zero-span} = \frac{\text{measured zero-span} \times 65.5}{\text{sheet weight}}$$

Zero-span values which were corrected to a basis weight of 65.5 grams per square meter were then plotted as a function of yield (Appendix, Figure 45).

Before any relationships are derived from the zero-span tensile strength data, one must consider the precise conditions represented by Figure 45. In this presentation of the data, the zero-span values were determined at constant sheet weight. It is normally presumed that the lignin content of pulp contributes little to the zero-span tensile strength.

¹ Appendix, page 121

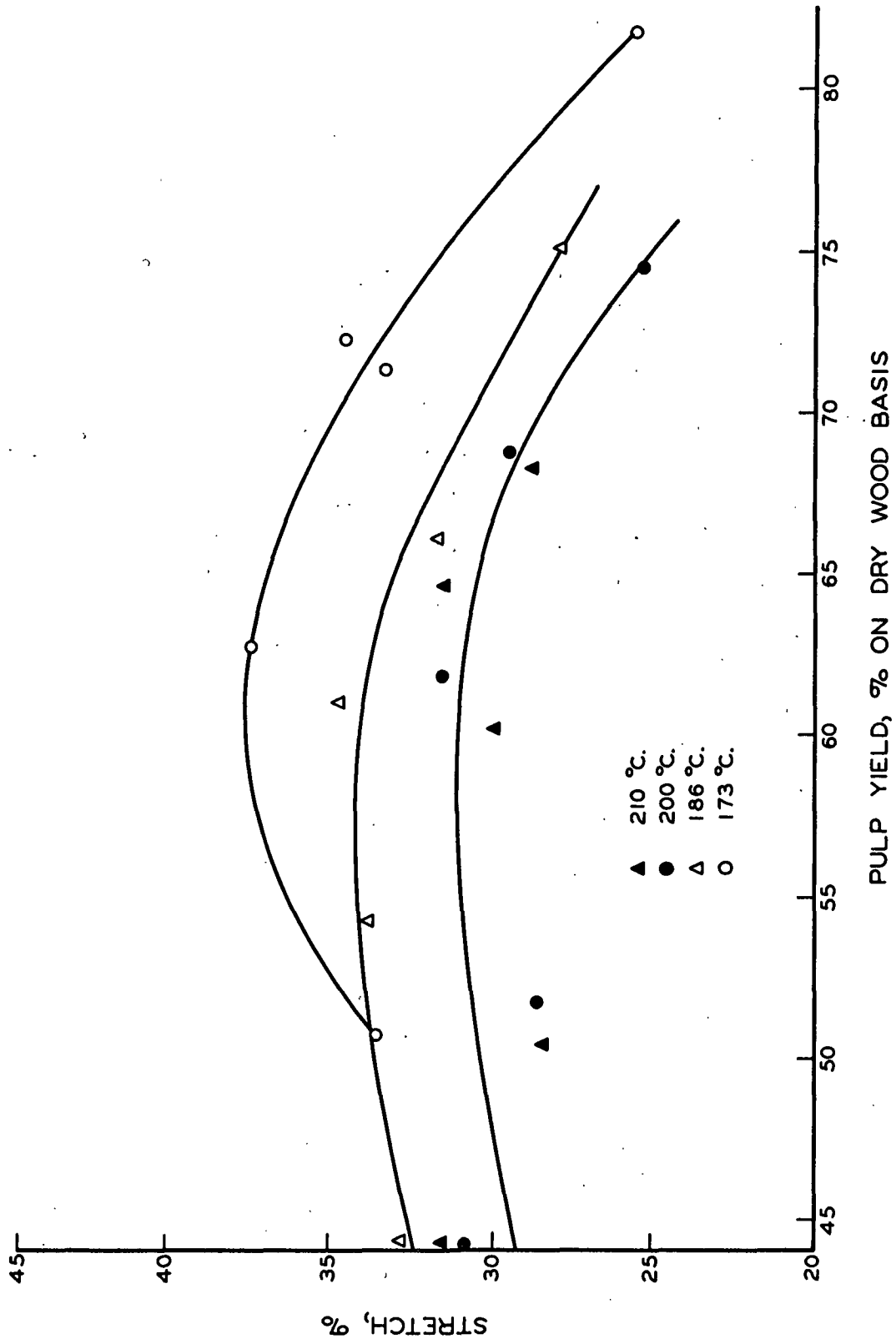


Figure 28. Stretch vs. Pulp Yield (10-Min. Beating Time)

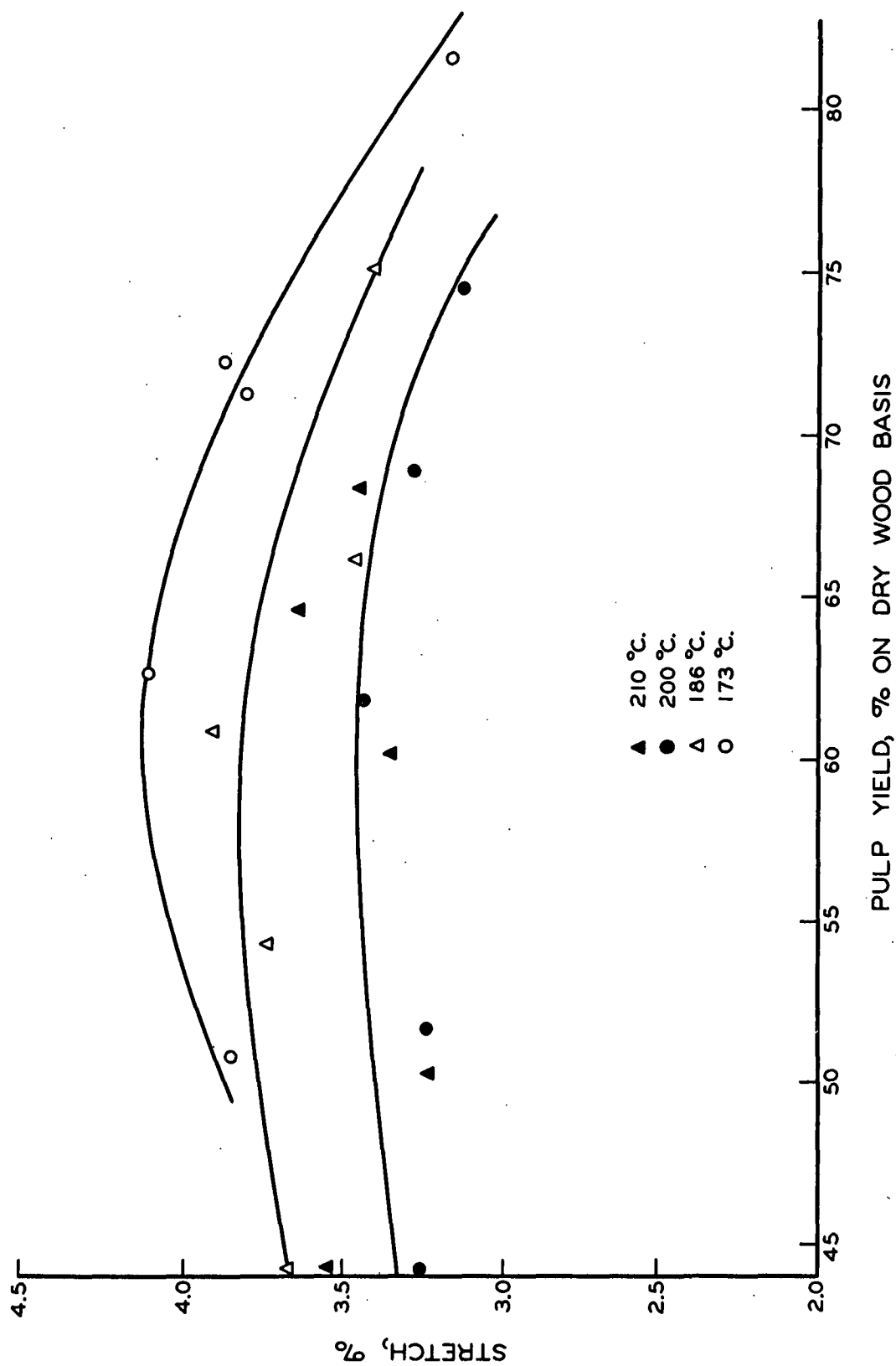


Figure 29. Stretch vs. Pulp Yield (20-Min. Beating Time)

TABLE VIII

Zero-Span Tensile Strength
(Measured at 10 min. beating interval)

Pulping Temperature 173°C.

Cook No.	Yield, %	Zero Span, lb./in. ^a	Corrected Zero Span, lb./in. ^b
32	81.7	49.56	61.51
31	72.3	58.76	67.69
29	71.3	59.41	69.22
39	62.7	61.00	66.86
33	50.8	54.55	56.60

Pulping Temperature 186°C.

Cook No.			
34	75.1	56.18	68.38
36	66.1	58.49	67.09
35	61.9	60.85	66.97
38A	54.3	57.94	60.82
37	44.0	49.61	51.34

Pulping Temperature 200°C.

Cook No.			
40	74.5	53.13	64.75
42	68.9	58.36	68.41
43	61.8	60.31	67.69
44	51.7	58.15	60.80
41	44.1	50.10	51.59

Pulping Temperature 210°C.

Cook No.			
47	68.2	54.23	63.75
46	64.6	57.97	65.46
49	60.1	54.35	60.45
48	50.3	49.82	52.68
45	43.9	48.51	50.41

^a Zero span reported in terms of pounds per inch per basis weight of 65.5 g. per sq. m.

^b Corrected zero span reported in terms of pounds per inch per cellulosic weight of 65.5 g. per sq. m.

Hence, when studying pulps of varying chemical compositions, it is probably more desirable to compare zero-span at constant carbohydrate weight. For this reason, the data was adjusted by assuming a direct proportional relationship between carbohydrate content and zero-span strength. A plot of the corrected zero-span tensile strength data can be found in Figure 30.

Figure 30 showed that at any given yield, the corrected zero-span tensile strength was approximately the same for pulps produced at temperatures of 173, 186, and 200°C. The data for these three isotherms did contain considerable scatter but it was considered that the zero-span measurements and methods for correcting for sheet weight and lignin content variations were insufficiently sensitive to detect the small changes that might have occurred in intrinsic fiber strength. However, a marked decrease occurred in the corrected zero-span tensile strength for pulps produced at 210°C. This decrease in corrected zero-span was significant, and indicated a decrease in intrinsic fiber strength at elevated temperatures of 5 to 10%.

OPACITY

The Bausch and Lomb contrast ratio was determined on all handsheets¹, and the results can be found tabulated in Table VII. Theoretically, an increase in fiber-to-fiber bonding would decrease sheet opacity. Thus, increased beating should, and actually did, decrease the measured opacity.

¹ Appendix, page 121

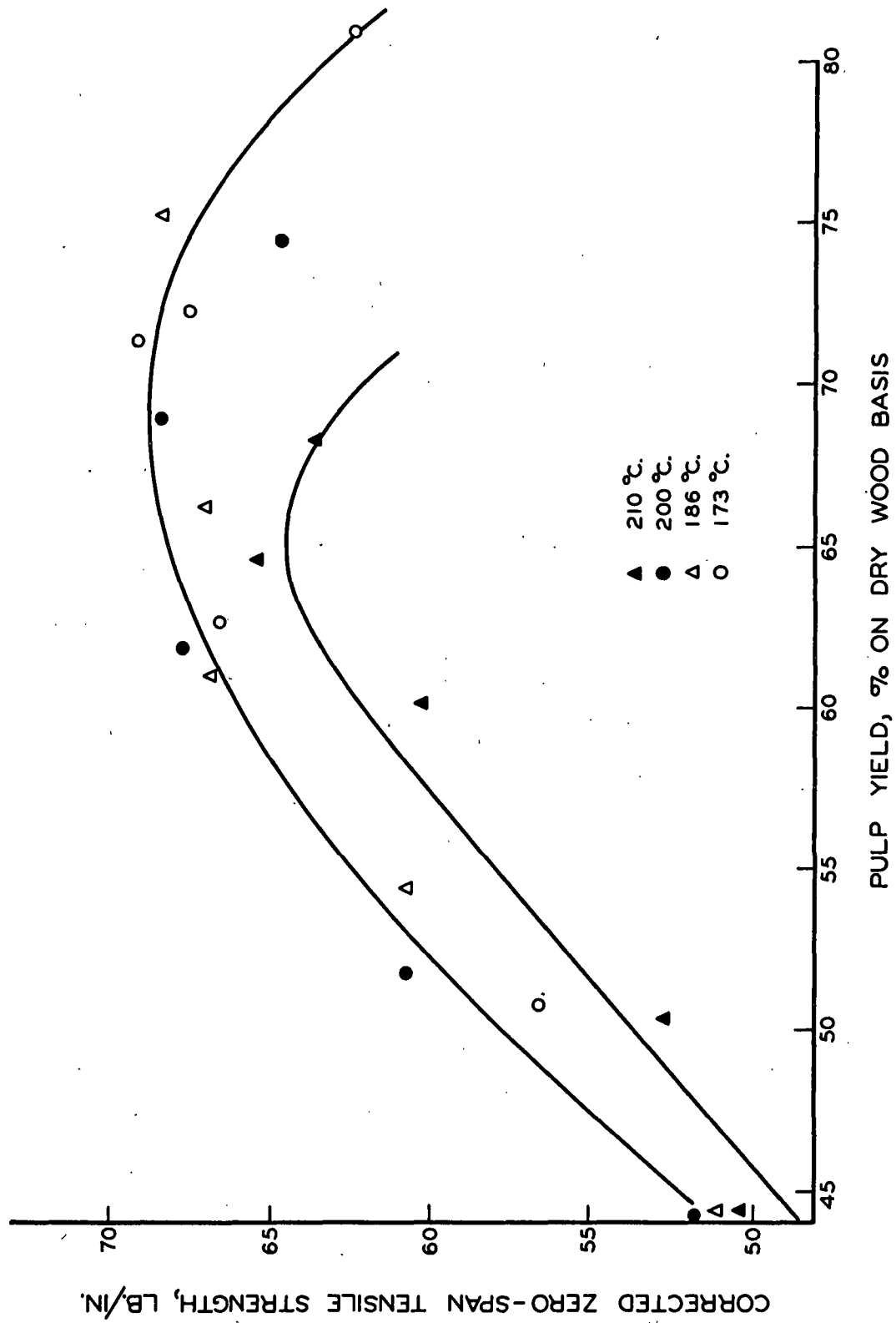


Figure 30. Corrected Zero-Span Tensile Strength vs. Pulp Yield

Opacity was plotted against yield at constant beating time, and a typical example of the plots obtained can be found in Figure 31. Although the data did not produce precise relationships in these plots, certain definite trends were observed. Opacity at a given beating time appeared to be almost independent of yield, but a temperature effect between opacity isotherms existed. Increasing pulping temperature increased sheet opacity when comparisons were made on the basis of equivalent yield and beating time.

RIGIDITY

The Clark rigidity factor was determined on the handsheets at all beating intervals¹. The measured values obtained can be found tabulated in Table VII. The data were analyzed in the manner previously described, that is, rigidity was plotted against beating time, and then plotted against yield at constant beating time. In plots of rigidity versus beating time, much more scatter existed in the data than was observed for other physical tests, and this erratic behavior was probably due to the fact that the Clark rigidity factor determination is not a precise test. When comparing pulps of very similar properties, the precision of the Clark tester is probably not sufficient to differentiate between the pulps. However, in general there was a trend showing an increase in sheet rigidity with increased beating.

When rigidity was plotted as a function of yield at constant beating time, the data presented no apparent useful relationships. At any one

¹ Appendix, page 122

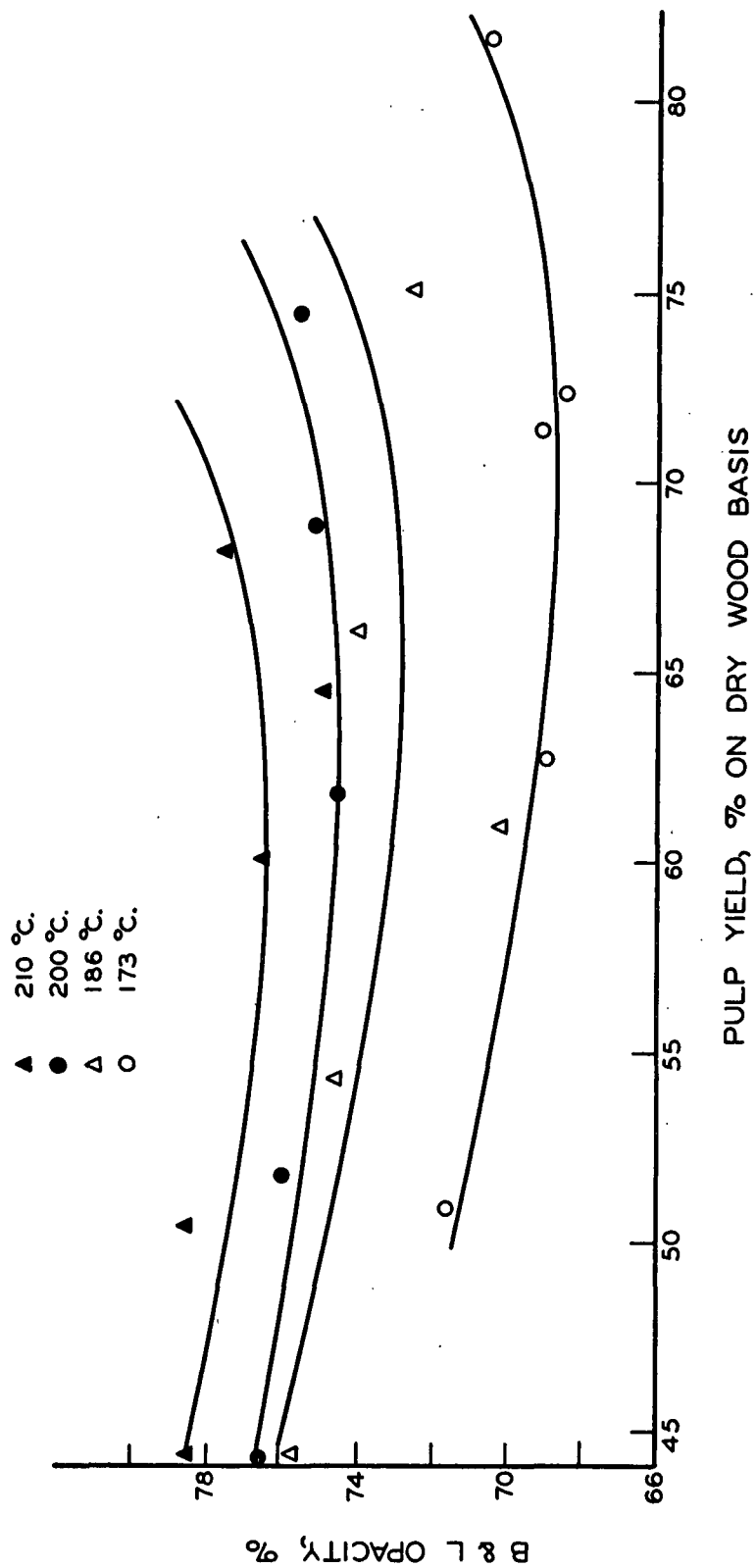


Figure 31. Opacity vs. Pulp Yield (10-Min. Beating Time)

pulping temperature, there appeared to be a relationship showing a decrease in sheet rigidity with increasing yield. However, there was no correlation between isotherms, and the effect of temperature appeared to be entirely random.

FREENESS

Schopper-Riegler freeness values were obtained and can be found tabulated in Table VII. These values have been empirically corrected for minor temperature and consistency variations. As expected, freeness decreased with beating; however, when freeness was plotted against yield at constant beating times, the data were quite erratic.

In an effort to compensate for some of this variability, plots of freeness versus yield at constant tensile strength were made (Figure 32). These plots showed smooth relationships, and provided the following information. High-temperature pulps beaten to the same tensile strength tended to have a lower freeness, regardless of yield. Furthermore, the differences in freeness related to pulping temperature appeared to be a function of yield. In the low-yield range, below approximately 55%, and in the high-yield range, above approximately 65%, the drainage properties of high-temperature pulps were markedly lower.

The variations in temperature effect on freeness with yield were probably the result of the shape of the tensile strength versus freeness curves. Tensile strength, itself, was a function of yield, with maximum tensile strength being obtained at yields of approximately 60% (Figure 26). At either higher or lower yields, tensile strength decreased.

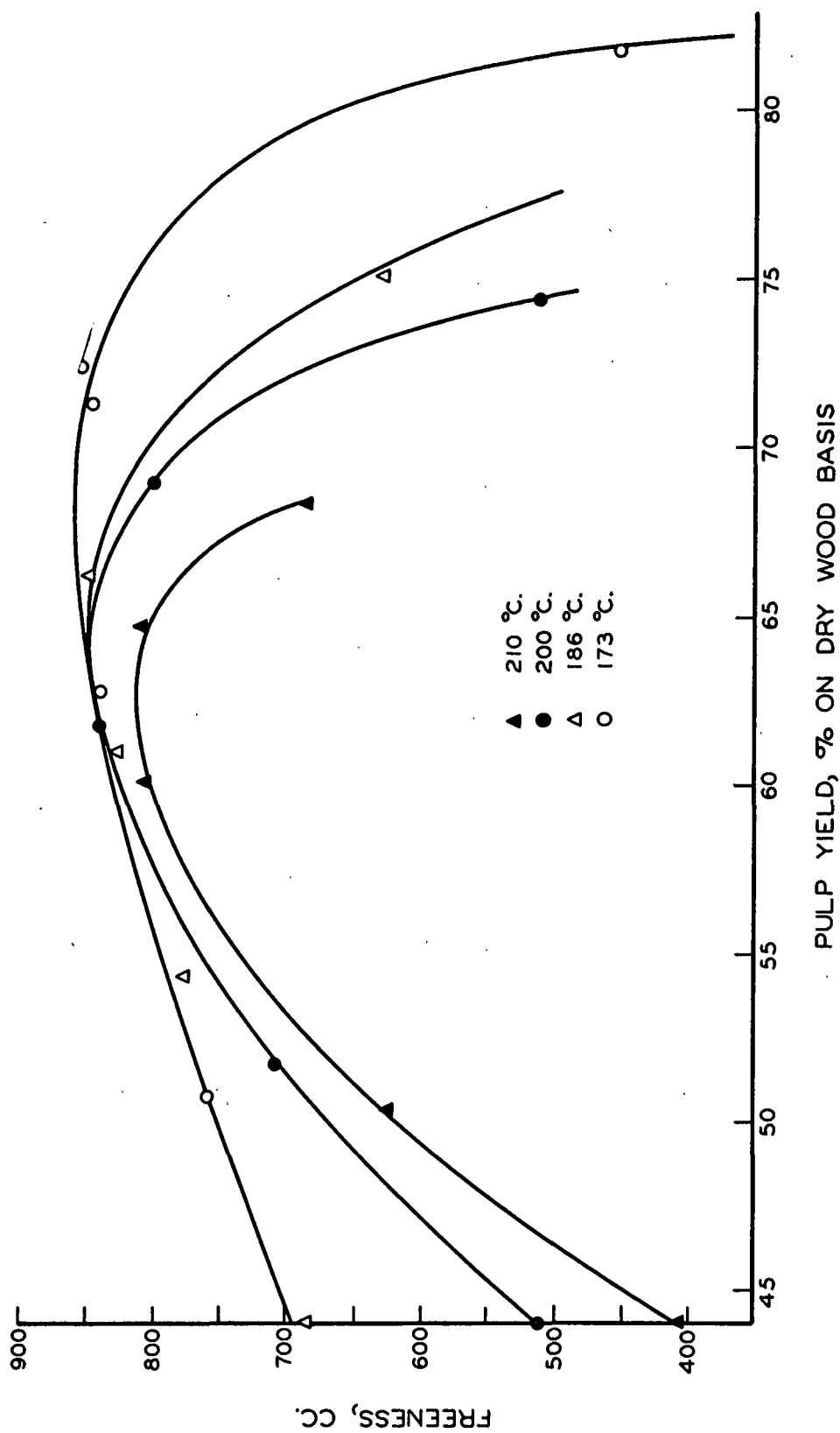


Figure 32. Freeness vs. Pulp Yield (Constant Tensile Strength 36 lbs. Per Inch)

Figure 33 portrays an idealized drawing representing these facts in a plot of tensile versus freeness. Such a plot would be obtained for pulps produced at any pulping temperature. Line (a) on Figure 33 is a line of constant tensile at a level very similar to that chosen for comparisons of freeness versus yield at constant tensile.

This value was chosen as

it represented the maximum constant tensile strength line which would intersect every constant yield line on the tensile-freeness plot.

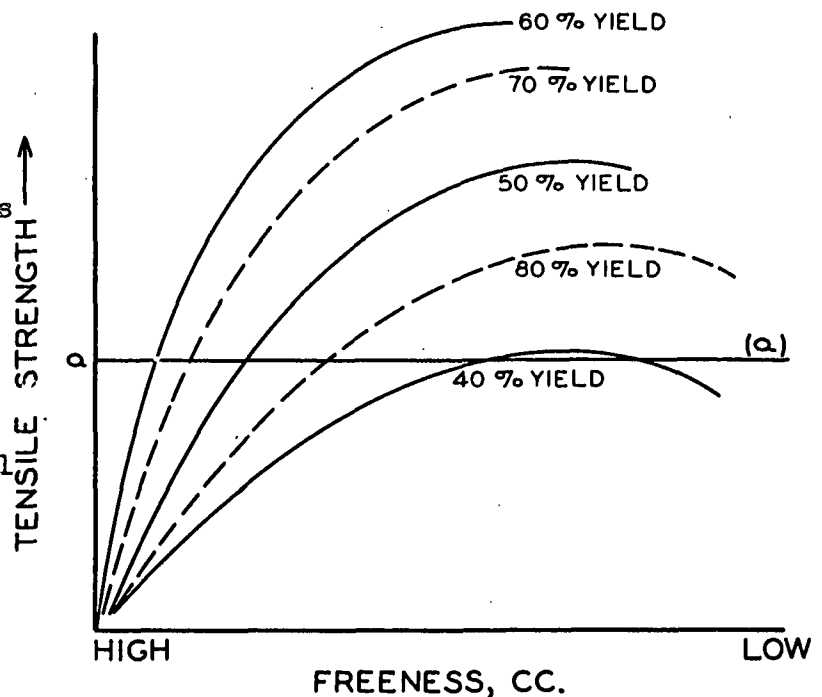


Figure 33. Tensile Strength vs. Freeness

It is important to note the rate of development of tensile strength with decreasing freeness at the points where the constant tensile line (a) intersects the various constant yield lines. With the high-strength pulps, this intersection occurs early in the beating cycle where the rate of change of tensile with decreasing freeness is great. With low-strength pulps, the intersection occurs where the rate of tensile development is low. It is this difference in the points of intersection which can be used to explain the results obtained in Figure 32.

For simplification, consider only four pulps and their respective tensile-freeness relationships (Figure 34). Two of the pulps are high-strength pulps of approximately equivalent yield, but these pulps differ from one another in temperature of pulping. The other two are similar to the first, except that they are low-strength pulps.

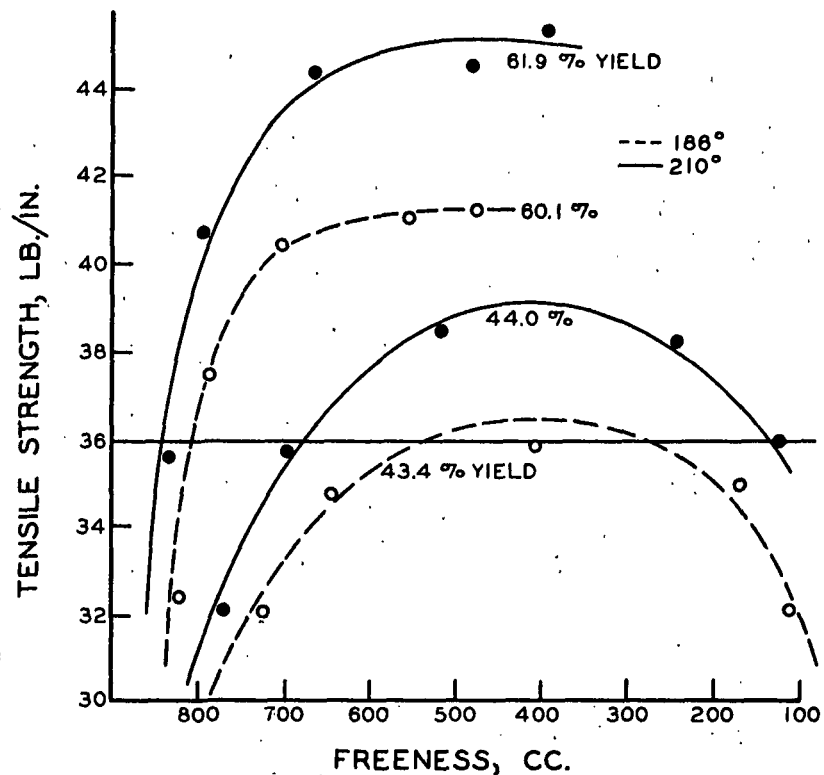


Figure 34. Tensile Strength vs. Freeness

If a line of constant tensile cuts through these plots, the following will be noted. Even though the temperature effect on tensile-freeness relationships for the high and low-strength pulps was approximately equivalent, comparisons at constant tensile would indicate greater freeness differences due to temperature in the case of the low-strength pulps. This was precisely what was observed from Figure 32.

As mentioned in the introduction¹, one cannot completely evaluate pulp characteristics without considering all three fundamental properties, namely: drainage, power requirements, and physical properties. Figure 32 represents a measure of drainage at a constant physical property, and,

¹ See page 53

for completeness, a graph of power requirements (equivalent to beating time in this thesis¹) at the same constant physical property should be prepared. This was done, and the graph can be found in Figure 35.

Figure 35 showed that the power requirements to produce a given tensile were influenced by temperature of pulping. Pulps produced at higher pulping temperatures require more extensive beating than do low-temperature pulps of corresponding yields. The differences in power requirements at various yield levels related to the temperature effect was explainable by reasoning identical to that presented for the explanation of tensile-freeness-yield relationships.

The method of analysis used for freeness and power requirements at constant tensile was repeated for constant tear and identical conclusions were derived. Hence, it was felt that some value might exist in comparing tear and tensile strength. This was done using the tensile-tear data representing strengths of 60% yield pulps. Figure 36 is a plot of tear factor versus tensile strength at 60% yield. It should be noticed that the tensile-tear ratios of pulps produced at various temperatures overlap in many instances. This means that much of the decreased strength of the high-temperature pulps can be recovered by increased beating², yielding sheets of the same tensile-tear strengths existing in sheets of less beaten, low-temperature pulps. However, it should also be noted that maximum developed tensile strength is less for the high-temperature pulps than for the low-temperature pulps. The highest tensile that was developed with the 210°C. pulp was about

¹ See page 53

² See page 54

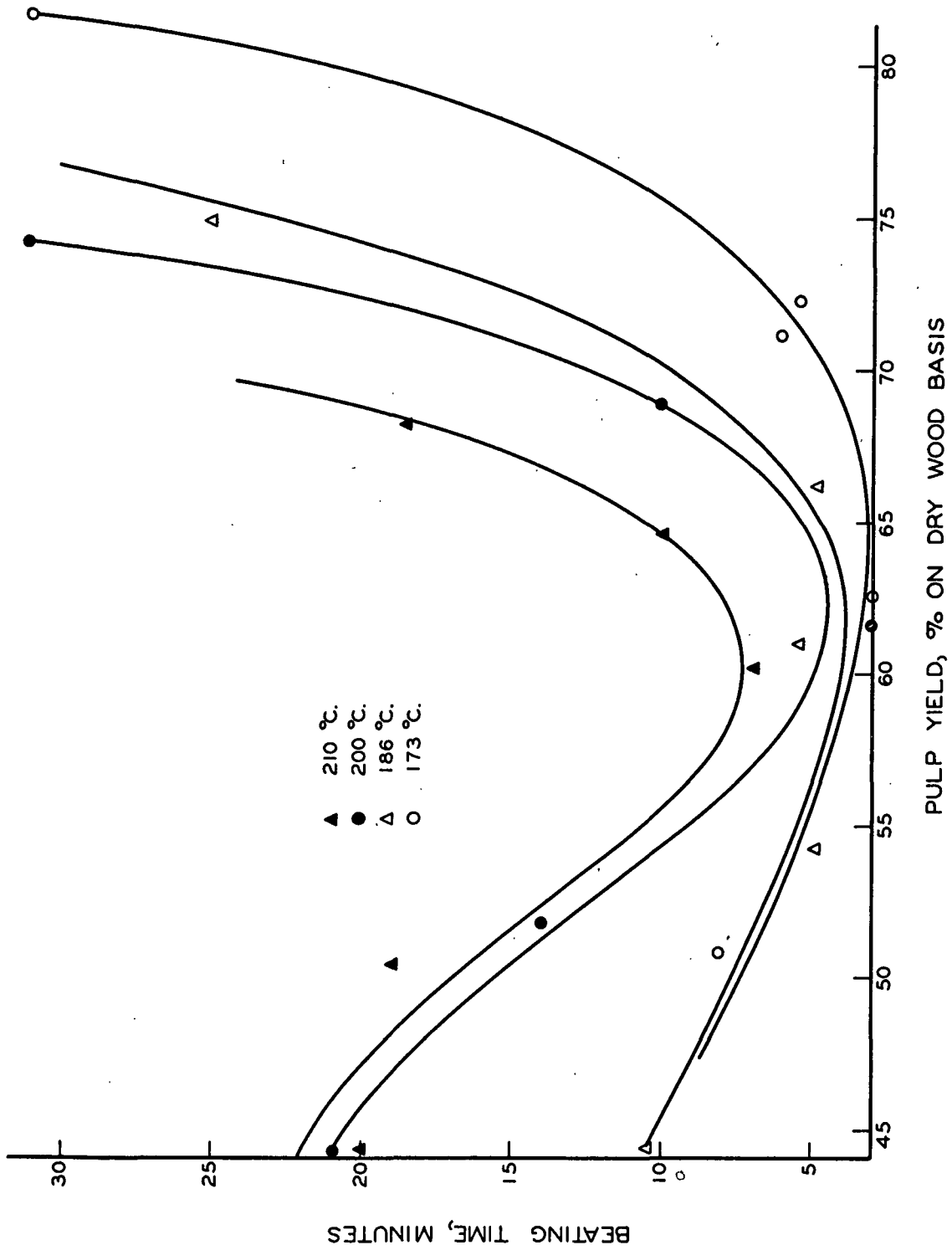


Figure 35. Beating Time vs. Pulp Yield (Constant Tensile Strength at 36 lbs. Per Inch)

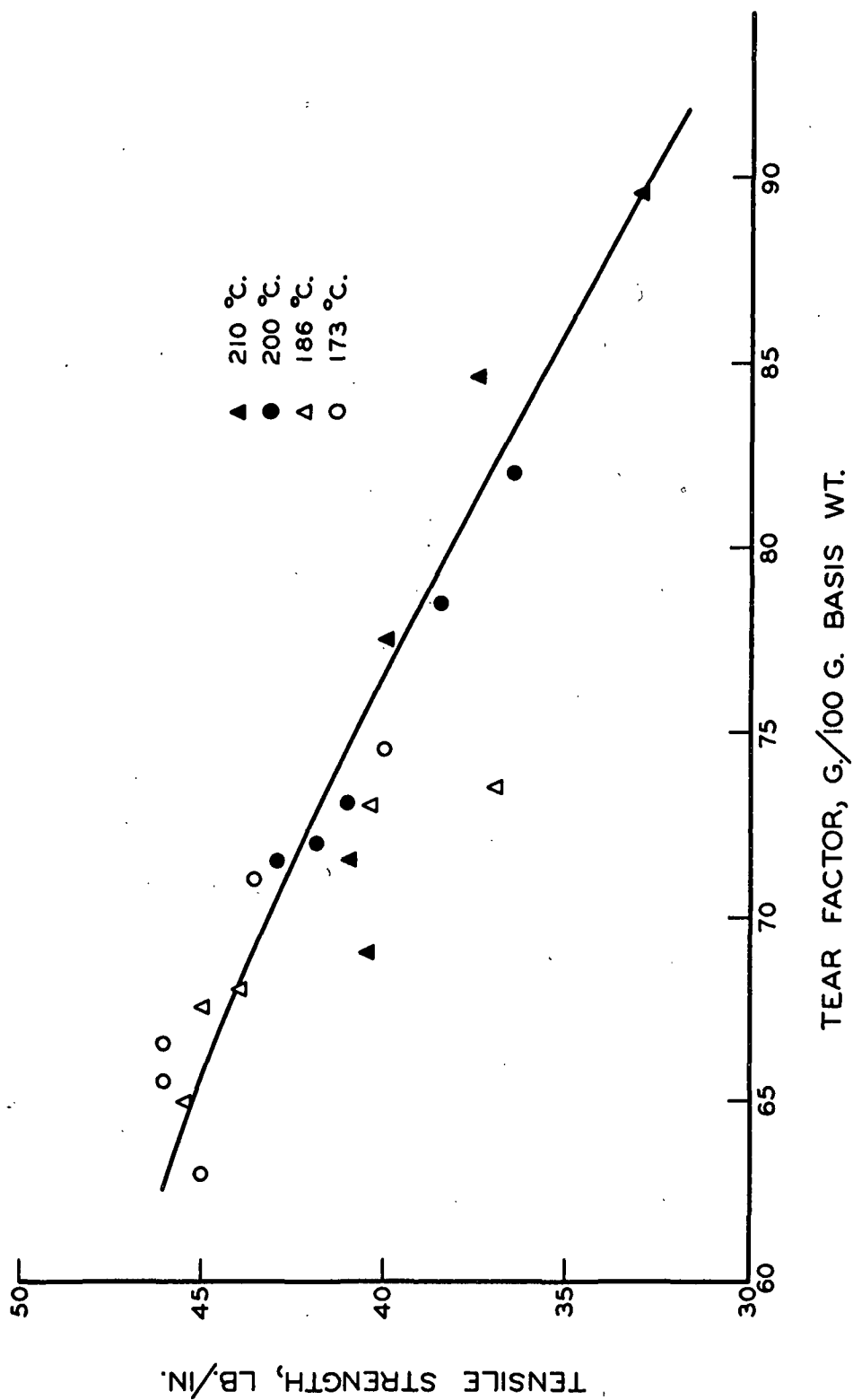


Figure 36. Tensile-Tear Relationship (60% Yield Pulp)

40 lbs. per inch. The maximum tensile that was developed with the 173°C. pulp was about 47 lbs. per inch. This tensile of 47 lbs. per inch was not obtained with the 210°C. pulp, regardless of the degree of beating or the amount of tear sacrificed.

DISCUSSION OF RESULTS

INTRODUCTION

In this thesis, data were obtained to show the effects of pulping temperature in two distinct areas. One, tests were conducted to evaluate pulp chemical properties; and two, other tests were conducted to determine the changes in physical characteristics of sheets of paper made from the several pulps.

Before considering the results obtained from a chemical study of the various pulps, it is desirable to review briefly some of the known physical chemistry of pulping reactions. A pulping system does not contain uniform concentrations of the reactants. In many studies, uniform liquor concentration with chemical reaction occurring at a heterogeneous solid interface has been assumed. However, in the actual zone of reaction, the concentration of the liquid phase is probably not uniform, nor need it approach the concentration of the bulk solution. The concentrations of chemicals at the point of reaction are the concentration terms which determine rates of chemical reactions. These concentrations, in turn, are dependent upon diffusion rates, ion mobilities, and solubilities of reaction products.

To date, insufficient techniques have been developed to determine concentrations and activities at interfaces under the conditions of pulping. Without such information, any attempt to derive kinetic constants can be misleading. One cannot use the idealized formula for true

solutions to cover a heterogeneous reaction. It is the author's opinion that representation of experimental findings by use of such homogeneous equations are generalizations, with the relationships evolving often being fortuitous, or applicable to only a very narrow range of conditions (4, 13).

Because of this lack of knowledge about the heterogeneous pulping reaction, no true theoretical kinetic study will be attempted in this thesis. In a few cases, a strictly empirical approach will be utilized. Such an approach may provide great utility, but because of the lack of fundamental considerations, the information resulting may not be applicable to any system except the exact one under study.

CHEMICAL ASPECTS

The question of adequate liquor penetration under the conditions employed in this study was of primary concern. The brightness data showed that this penetration must have occurred very rapidly. The pulps produced in the isothermal digester were unusually white, and increasing pulping temperature did not markedly change pulp brightness. Even a small amount of burning which would have resulted from a lack of penetration would have lowered the brightness values considerably.

One possible, but unproven, hypothesis for the lack of burning is the following. Under the conditions employed in this thesis, the wood was surrounded by liquor at cooking temperature almost instantaneously. Heat could penetrate into the chip by only two processes, by conduction

or by moving in with the hot liquor as liquor penetration was accomplished. If the rate of conduction were slower than the rate of penetration, it would have been impossible for any of the wood to reach elevated temperatures while not in intimate contact with cooking liquor. In several cooks, typical mill chips (measuring one by one by one-quarter inch) were included in the charge of veneer chips. Examination of these sapwood chips failed to show any burning. Thus, even conventional chips appeared to be adequately penetrated under the conditions of this study.

Pulp yield is not a true chemical property, but accurate yield figures are necessary when considering over-all rate effects. The yield data showed that cooking temperature has a very great effect on rate of pulping. As the cooking temperature increased, the over-all pulping reaction rate was greatly accelerated. For example, the time required to produce a pulp of 50% yield at 210°C. was only one-fifteenth the time required to pulp to the same yield at 180°C. (The common approximation of assuming a doubling in rate for each 10°C. increase in temperature predicts that the elevated temperature should require one-eighth the pulping time.) An empirical approximation of the temperature effect on the over-all rate of pulping can be found in the Appendix (page 127). This approximation was derived for the calculation of equivalent cooking time.

In order to show the great effect of cooking temperature on rates of reaction, a rectangular plot of pulping temperatures versus pulping time was prepared and can be found in Figure 37. This temperature-yield-time plot is important, as it also emphasizes the requirements of accurate

control of temperature and cooking time. At pulping times greater than 3000 seconds, a variation in cooking time of approximately 300 seconds affected the yield by less than 1%. A similar variation in pulping time at elevated temperatures would affect the yield value as much as 20%. Similarly, the importance of temperature is apparent. At elevated temperatures, a 1°C. variation in cooking temperature can cause the final pulp yield to vary by several per cent. However, with proper control, no difficulties were encountered in pulping to any yield value in the temperature range studied.

The primary purpose of pulping is chemical delignification with a minimum removal of carbohydrates. Hence, the temperature effect on the reactions leading to lignin removal become extremely important. Measurements of both total lignin (Klason lignin plus UV lignin) and pulp methoxyl content showed that increasing pulping temperature tended to decrease the total amount of lignin removed (by about 1% over the temperature range studied) when comparisons were made at constant yield levels.

The total lignin determination, itself, is influenced by many variables, and it was felt advisable to obtain an indication of the effectiveness of this determination. This was done by calculating the per cent methoxyl based on the total lignin present, and comparing these values with reported lignin methoxyl contents (35, 36, 37). The calculated total lignin methoxyl content for all the pulps can be found in Table IX. In all cases where the measured total lignin exceeded 3%, the per cent methoxyl based on the total lignin content varied between 25 and 29.8%,

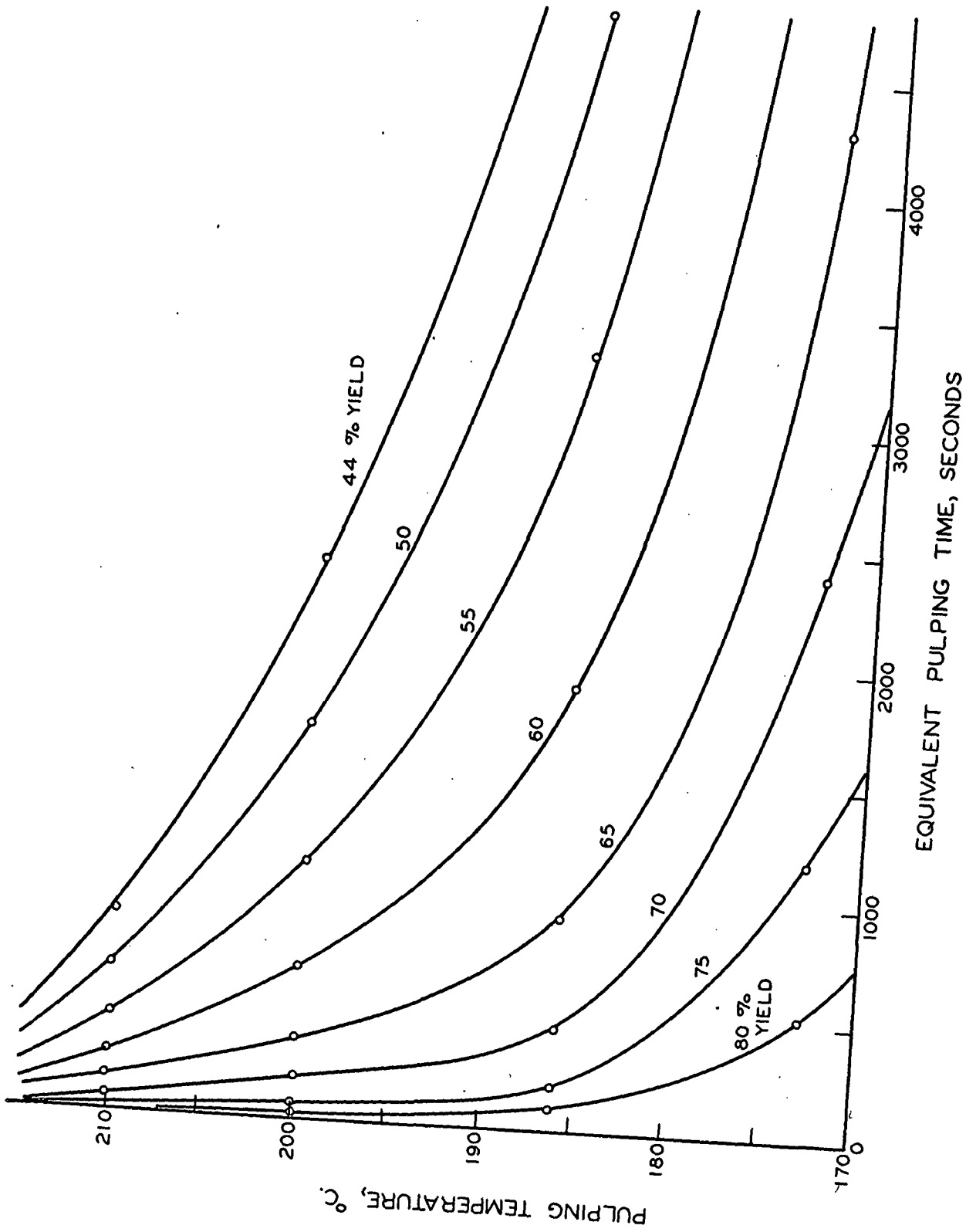


Figure 37. Pulping Temperature vs. Cooking Time at Constant Yield

with the average being 26.2%. This average value of total lignin methoxyl content was considerably higher than the normally reported aspen lignin methoxyl content (20.0 to 22.0%). While it is true that neutral sulfite pulps contain nonlignin methoxyl compounds, it is unlikely that such compounds would account for 5% of the total methoxyl present (38).

The reason for not considering total lignin methoxyl content of pulps containing less than 3% total lignin was based on considerations of the total lignin test procedure. It is well known that pure carbohydrate material will show pseudo-lignin content from the ultraviolet absorption figures (39). Furthermore, the total lignin determination is not a test of high precision, and precision drops off quite rapidly in the area of low lignin content. With pulps low in lignin, a very small difference in the measured total lignin would result in a comparatively large percentage difference in the total lignin methoxyl content.

The total lignin content was determined on alcohol-extracted pulps, while the methoxyl content was based on pulp which had only been water-washed. Thus, there was a possibility that the alcohol extractives contained methoxyl-bearing compounds, and, hence, were responsible for the abnormally high total lignin methoxyl content. Secondary evidence of this possibility lies in the following. It was observed during the process of making the alcohol extractions that the extractives of pulp were of an entirely different nature than those from a similar extraction of wood. The wood extractive was a light brown in color, showed signs of being in true solution, and upon drying yielded a glossy waxlike substance.

TABLE IX

METHOXYL CONTENT

	Cook No.	Lignin on Pulp Basis, %	Extrac- tives on Pulp, %	Methoxyl on Pulp, %	Methoxyl on Total Lignin, %	Methoxyl on Possible Lignin, ^a %
173°C.	32	17.3	2.1	4.43	25.6	22.8
	31	11.3	1.9	2.92	25.8	22.1
	29	12.3	1.9	3.14	25.6	22.0
	39	7.0	1.8	1.87	25.3	21.2
	33	1.8	1.8	.57	31.6	15.8
186°C.	34	15.6	2.2	3.90	25.0	21.9
	36	10.1	2.7	2.68	26.5	21.0
	35	6.7	2.4	1.85	27.6	20.4
	38A	3.0	1.8	.88	29.4	18.3
	37	1.2	2.2	.30	25.0	8.8
200°C.	40	15.8	2.2	4.09	25.9	22.7
	42	12.2	2.5	3.07	25.2	20.9
	43	8.7	2.2	2.20	25.3	20.2
	44	2.4	2.0	.75	31.4	17.1
	41	1.3	1.6	.03	2.3	1.3
210°C.	47	11.9	3.0	3.14	26.4	21.1
	46	8.6	2.8	2.56	29.8	22.5
	49	7.4	2.7	2.01	27.2	20.0
	48	3.2	2.2	.77	24.0	14.3
	45	2.0	1.8	.03	1.8	.8

^a Total lignin plus extractives equals possible lignin content.

The pulp extractives, on the other hand, appeared to be in colloidal suspension, and were a light green to pink in color. The red coloring matter which was discussed earlier in this report¹ was completely removed in the process of alcohol extraction. The pulp extractives, when

¹ See page 50

evaporated to dryness, yielded a greenish-brown solid, which unlike the wood extractive, was highly hygroscopic.

Stone (21) extracted neutral sulfite aspen pulps with alcohol and carried out nitrobenzene oxidations on the dried extract. This gave high yields of vanillin and syringaldehyde, with the syringyl-to-guaiacyl ratio being higher than normal.

All this secondary evidence tends to support the theory that alcohol extractives of pulps contain substances whose precursor was lignin material. If this were the case, it would then be quite likely that the extractives would have a considerable methoxyl content. Ideally, the methoxyl content of the extractives should have been experimentally determined. However, the extractive material had been discarded before any appreciation of the value of a methoxyl determination was obtained. It was necessary, therefore, to consider the effect of extractive methoxyl content by a secondary and less desirable procedure.

For the sake of discussion, it was assumed that all the pulp extractives were ligninlike materials. The amount of total lignin plus extractives was calculated, and this figure was termed "possible lignin" content. The values of the possible lignin methoxyl content were calculated and can be found in Table IX. Again eliminating those pulps which contain less than 3% lignin, the possible lignin methoxyl content was found to vary between 22.8 and 20%, with the average being 21.4%. This mean figure was well within the limits of reported aspenwood lignin methoxyl content.

On the basis of the various evidence and arguments presented relating total lignin, extractives, and methoxyl content of the pulps, the following hypothesis is presented. Pulping at increased temperature slightly increases the amount of total lignin and alcohol extractives remaining in the pulp. The alcohol extractives contain a portion of ligninlike material which has been made alcohol-soluble during pulping but which remains water-insoluble. The portion of lignin which is so altered increases slightly with increasing pulping temperature. It may be that this small portion of alcohol-extractable altered lignin was responsible for most of the adverse color reactions observed in the pulps.¹

As mentioned previously, the greatest effect of increasing pulping temperature was on the over-all rate of pulping. To show the rate effect on lignin removal, a plot of total lignin content versus corrected time of pulping was made (Figure 38). Increasing temperature greatly accelerated the rate of lignin removal, and in all probability, this increase in rate of reaction is related exponentially with temperature. Efforts to find a simple correlation relating lignin content, time of reaction, and temperature of pulping were only partially successful. Apparently, the complexity of the system could not be described by a simple expression.

In examining the original data, the total lignin contents for various yields and temperatures were determined from Figure 10. The rate of lignin removal at each point was then determined by measuring the slope

¹ The nitrobenzene oxidations performed by Stone suggest the presence of lignosulfonic acid in the extractives which could possibly oxidize to quinones, giving various color reactions.

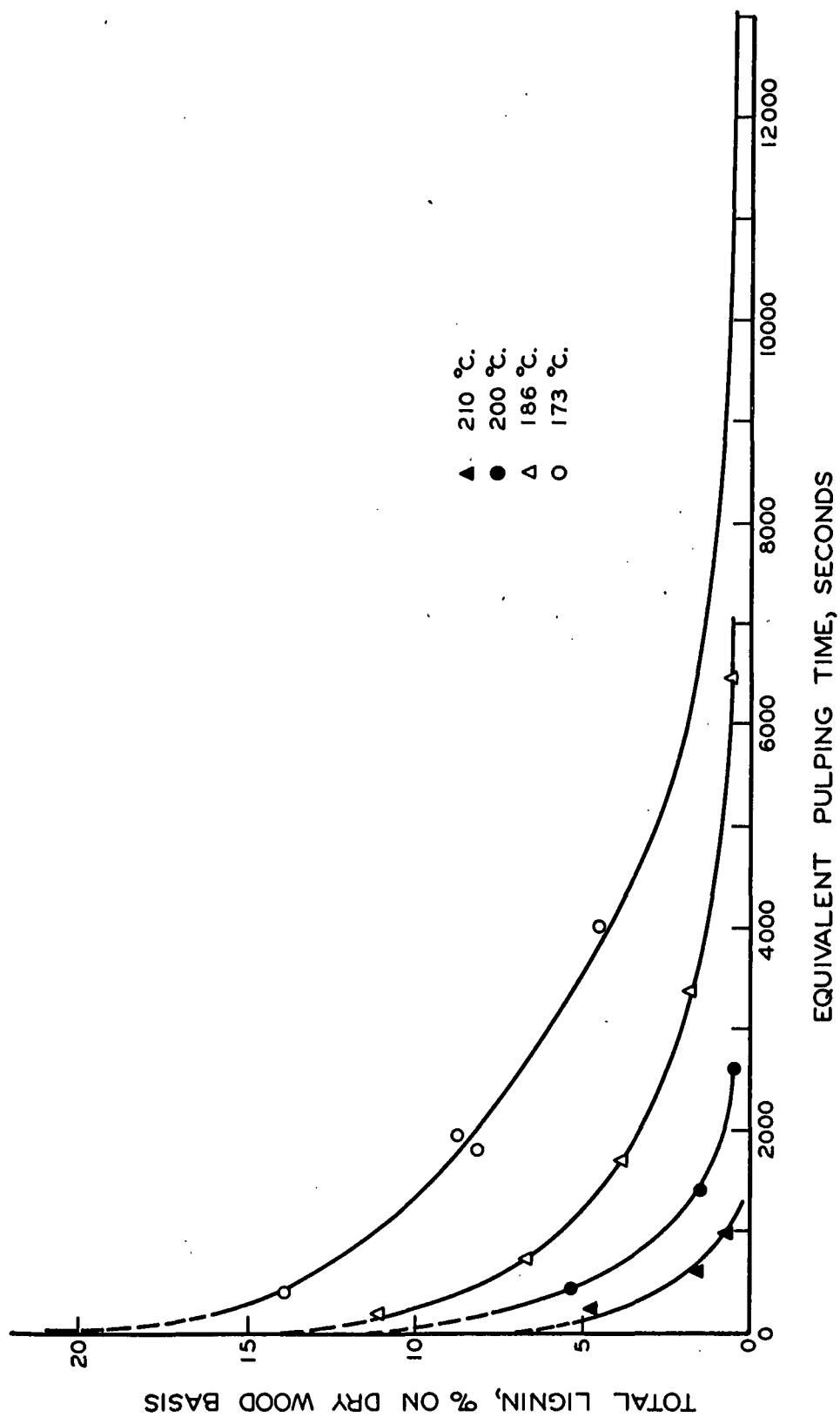


Figure 38. Total Lignin vs. Pulping Time

of the curve in Figure 38 at the appropriate total lignin content and temperature. The measured rates of reaction thus obtained can be found tabulated in Table X. Because of the large change in rates of reaction, it was felt advisable to plot the variables on semi-log paper. It was found that when the log of the rate of reaction was plotted against the reciprocal of temperature in absolute terms, a family of curves was obtained relating rate, yield, and temperature. Such a plot can be found in Figure 39.

The fact that a high-temperature pulp contains slightly more lignin than does a low-temperature pulp of the same yield means, correspondingly, that the high-temperature pulp must contain less carbohydrate material. Holocellulose determinations on the pulps substantiated this conclusion, as it was found that over the 37°C. temperature range studied, the high-temperature pulps contained from 1 to 2% less holocellulose.

Holocellulose is, however, not a simple constituent of wood or pulp but rather is a mixture of many different carbohydrate polymers. Therefore, it was important to determine the temperature effect not only on holocellulose but also on the various carbohydrate fractions within the holocellulose portion of the pulp. Measurements of the amount of holocellulose which was insoluble in 10 and 21.5% sodium hydroxide solutions showed that the alkali-resistant portion of the holocellulose was essentially independent of any temperature effect. Temperature of pulping appeared to have an effect only on that carbohydrate material which was soluble in alkali. Higher pulping temperatures decreased the amount of

TABLE X

REACTION RATES OF LIGNIN REMOVAL

Yield, %	dc/dt at 173°C.	dc/dt at 186°C.	dc/dt at 200°C.	dc/dt at 210°C.
45	.000??	.000??	.00036	.00080
50	.000??	.00051	.00135	.00370
55	.00056	.00113	.00340	.00643
60	.00133	.00234	.00606	.01180
65	.00185	.00425	.01040	.02845
70	.00220	.00897	.02255	.07850
75	.00328	.02270	.04230	.11100
80	.00553	.04000	.08000	--

dc/dt represents the over-all rate of lignin removal, where t is in seconds and c is in percentage total lignin.

alkali-soluble material remaining in the pulp. Pentosan determinations (most pentosans being alkali-soluble) substantiated this trend, as high-temperature pulps showed a markedly lower pentosan content.

While the experimental data showed that the amount of alkali-resistant carbohydrate remaining in the pulp appeared to be independent of pulping temperature, there were certain changes in the alkali-resistant fractions. An indication of the degree of polymerization was obtained through viscosity measurements. The cupriethylenediamine viscosity of the holocellulose fraction decreased markedly in pulps produced at higher cooking temperatures.

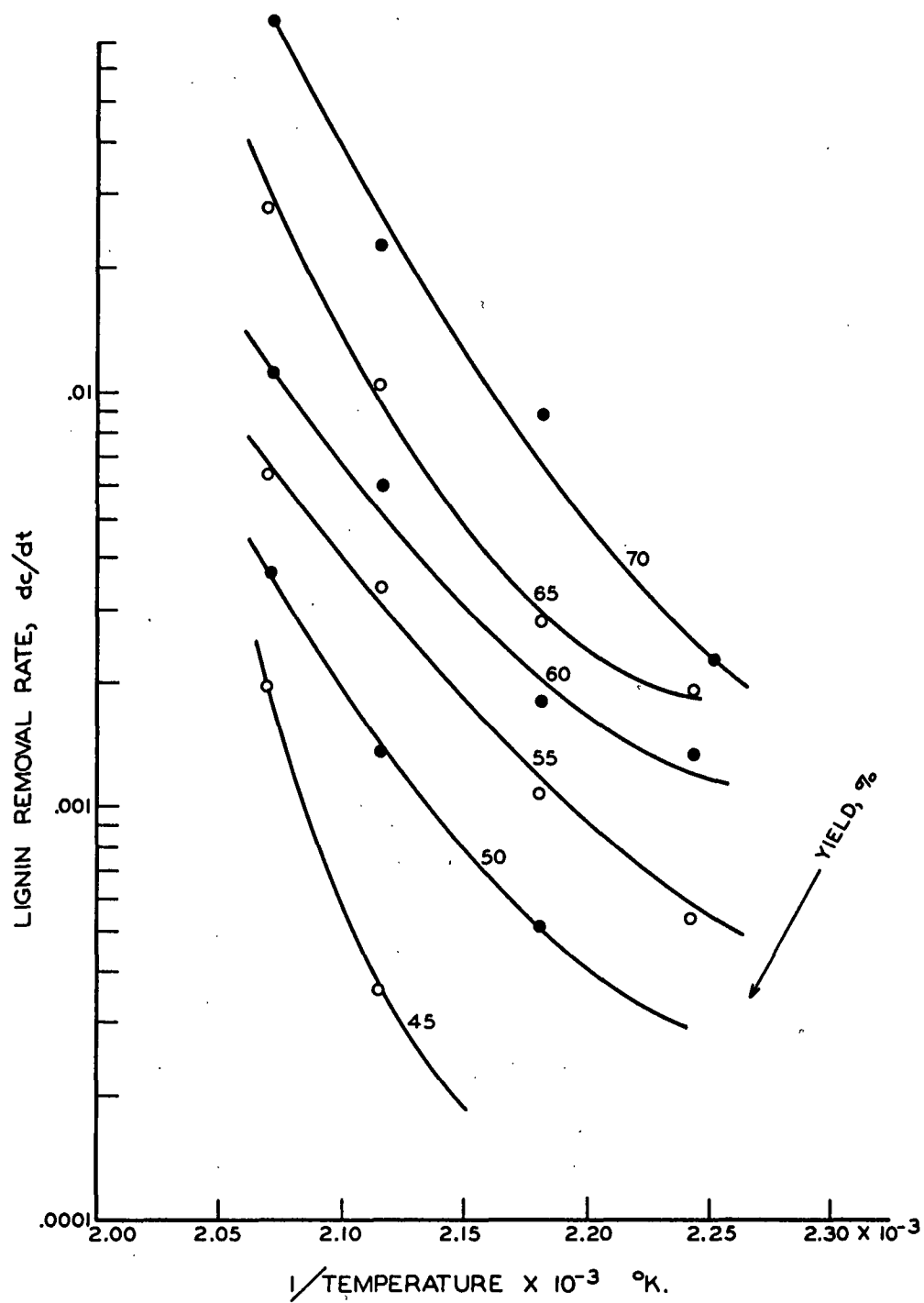


Figure 39. Log Lignin Removal Rate vs. Reciprocal Absolute Temperature

Thus, it must be concluded that the long-chain molecules originally present in the wood were degraded to a greater extent by high temperature, but this degradation was not sufficient to make them soluble in alkali.

In conclusion, it was felt that the chemical characteristics of the various pulps and the changes related to the temperature effect could be best explained by the following hypothesis. Under the conditions of cooking employed in this thesis, liquor penetration without chip burning occurred throughout the wood almost instantaneously. As the pulping temperature was increased, the over-all pulping reaction rate was greatly accelerated. There appeared to be an indication of a slight decrease in the rate of lignin removal relative to the rate of cellulosic removal. Hence, when pulping to the same lignin content, slightly greater cellulosic removal and degradation occurred at higher temperatures than at lower temperatures. However, it must be remembered throughout this discussion of chemical properties that only minor differences related to temperature effects were observed. With few exceptions, the differences were usually in the order of magnitude of 5% or less over the temperature range studied.

SHEET PROPERTIES

The measured change in density, zero-span tensile, stretch, and opacity values indicated that pulping temperature affected two basic sheet properties. Increasing pulping temperature decreased the fiber's intrinsic strength and its bonding capacity. However, as with the chemical properties, the temperature effect was small and usually amounted to less than a 10% change in sheet properties.

Evidence supporting the conclusion that increasing pulping temperature decreases fiber-to-fiber bonding capacity can be found from direct consideration of the changes noted in the density and opacity measurements. Theoretically, an increase in fiber-to-fiber bonding, as would occur with increased beating, should, and actually did, decrease opacity and increase density. The effect of pulping temperature, however, was the opposite of beating, and, hence, it was concluded that increasing pulping temperature probably decreased the pulp's fiber-to-fiber bonding capacity when comparisons were made at the same beating time.

Additional evidence indicating the effect of pulping temperature on fiber-to-fiber bonding capacity was found in the tear data. To interpret these trends, one must first review the mechanisms involved in the tear test (40). During tearing, energy is absorbed in either of two ways. That is, individual fibers are either broken or dragged intact from the fiber mesh. The tearing resistance or tear factor measured is a summation of the total energies (work) expended in both mechanisms. It is important to note that tearing resistance will be dependent not only on the amount of energy required to rupture or withdraw a fiber, but also upon the number of fibers broken or withdrawn.

A decrease in intrinsic fiber strength, as occurred at all pulping temperatures when pulping progressed below approximately 54% yield, resulted in a decrease in tear factor. (Later discussion of zero-span measurements will show that the intrinsic fiber strength decreased very rapidly as cooking progressed into the low-yield range.) As intrinsic

fiber strength decreases, the energy required to rupture a fiber decreases, and the number of fibers ruptured during tearing should increase. Both of these effects would lower tearing resistance.

A decrease in fiber-to-fiber bonding, on the other hand, decreases the drag resistance of the fibers and thereby decreases the likelihood of fiber breakage. If the drag resistance is less than the intrinsic fiber strength of a particular fiber, that fiber will pull out of the sheet without breaking. On the other hand, if the drag resistance is greater than the intrinsic fiber strength, the fiber will break. The energy consumed, or the work done in breaking a fiber, is generally less than that required to separate the fiber from the sheet, because the distance over which the force must act is lessened when the fiber breaks. Thus, a decrease in the amount of fiber breakage resulting from a decrease in fiber-to-fiber bonding will increase the energy consumed in tearing even though the force required to produce the failure may be decreased.

Zero-span and viscosity measurements indicated that high pulping temperature decreased the intrinsic fiber strength to some extent. This would, in turn, decrease tearing resistance. However, the observed fact was that tearing resistance increased with increasing pulping temperature. This must, therefore, be considered as evidence of lower fiber-to-fiber bonding capacity with high-temperature pulps.

Zero-span tensile strength decreased rapidly as pulping progressed to yields below approximately 70%. A similar change was observed in the

viscosity measurements and, hence, it was concluded that at all pulping temperatures the intrinsic fiber strength decreased as pulping progressed below about 70% yield. When comparisons were made at equivalent yields, no significant change in fiber strength was observed in zero-span measurements when pulping temperatures were increased to 200°C. However, as the temperature was increased further, the zero-span strength showed a marked decrease. This evidence, coupled with the trends shown by the cupriethylenediamine viscosity measurements presented a strong indication that high-temperature pulps (over 200°C.) decreased in intrinsic fiber strength.

The high-yield pulps exhibited relatively low tensile strength. This was undoubtedly due to the large amounts of lignin remaining in these pulps. Even though the intrinsic strength of the fibers in this yield range was probably preserved, lignin interfered with fiber-to-fiber bonding, resulting in a situation where strong fibers were poorly bonded to one another. The lack of fiber-to-fiber bonding resulted in a low tensile strength. As the pulping process progressed, lignin content was reduced, thereby promoting better fiber-to-fiber bonding. Simultaneously, there was a reduction in the intrinsic fiber strength, with the balance of the two factors being such as to provide increasing tensile strength until yield values approached approximately 60%. As pulping progressed to even lower yields, the loss in intrinsic fiber strength overshadowed the corresponding gain in fiber-to-fiber bonding, and tensile strength decreased.

The effect of pulping temperature on tensile strength (increasing temperature, decreasing tensile strength) was explainable by similar reasoning. High-temperature pulps apparently possess a lower intrinsic fiber strength and a lower bonding capacity. Both factors tended to promote a decrease in tensile value.

In summation; the tensile strength, tear factor, sheet density, and sheet opacity indicated that high-temperature pulps possessed a somewhat lower fiber-to-fiber bonding capacity than low-temperature pulps. This behavior would be expected from the relatively higher lignin content and lower hemicellulose content of the high-temperature pulps. Tensile strength, zero-span, and viscosity measurements indicated that high-temperature pulps have a slightly lower intrinsic fiber strength.

CONCLUSIONS

1. Increasing pulping temperature greatly accelerated the over-all pulping reaction rate of the neutral sulfite process.
2. The data indicated that pulps produced at high temperatures appeared to contain slightly higher percentages of residual lignin with a corresponding decrease in total carbohydrate material when compared on the basis of equivalent yields. Over a pulping temperature range of 37°C., the increase in residual total lignin amounted to approximately 1.0% throughout the yield range, at any given yield.
3. With respect to the chemical characterization of the pulps the following pulping temperature effects were observed.
 - a. Increasing pulping temperature decreased the amount of alkali-soluble material remaining in the holocellulose fraction at constant yield.
 - b. The percentage of alkali-resistant cellulosic material (on the wood basis) was not affected by pulping temperature, and was only a function of yield.
 - c. Increasing the pulping temperature substantially decreased the average degree of polymerization of the holocellulose fraction at constant yield.
 - d. Increasing the pulping temperature decreased the amount of pentosans remaining in the holocellulose fraction. Over the 37°C. range investigated, the pentosan content decreased by approximately one-third at constant yield.
4. The temperature effects observed on the physical tests on handsheets were relatively small. When pulps of equivalent yield were compared at the same beating times the direction of changes with increasing pulping temperature were:

- a. Increased tear factor
 - b. Decreased tensile strength
 - c. Increased opacity
 - d. Decreased brightness
 - e. Decreased stretch
5. In all cases the effect of pulping temperature on sheet characteristics was explained by considering that high-temperature pulps had a slightly lower intrinsic fiber strength and lower fiber-to-fiber bonding capacity at the same beating time than did low-temperature pulps.
6. The pulp strength differences that were related to fiber-to-fiber bonding as caused by pulping temperature change could be minimized, within limits, even for such inverse relationships as tensile-tear, by prolonging the beating of high-temperature pulps. However, this increase in strength was obtainable at a sacrifice in drainage properties as measured by freeness and an increase in power expenditure for beating.
7. Viscosity and zero-span measurements both indicated that intrinsic fiber strength was lowered as pulping temperature increased. The decreased holocellulose content, increased lignin content, decreased alkali-soluble carbohydrate material, and decreased pentosan content with increasing temperature of pulping were all in agreement with the observed lower fiber-to-fiber bonding capacity at the same beating

time exhibited by the high-temperature pulps in physical testing. Hence, throughout this work the results of the chemical analysis were in agreement with the behavior exhibited by the handsheets.

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APPENDIX I

CHIP BASKET DESIGN

The best way of describing the design of the chip basket is through use of the accompanying photograph (Figure 40). The outer shell of the basket (part 1) was constructed from a polished perforated 316 stainless steel plate. The perforations in this plate were such that the plate was quite porous to the flow of liquids but at the same time it tended to shield the contents of the basket from radiation from the hot digester walls.

The outside shell of the basket was constructed to a diameter smaller than the internal diameter of Digester No. 2. Transite tabs (parts 2) were fitted to the basket, and these tabs acted as spacers when the basket was placed in the digester. At no point did the basket make metal-to-metal contact with the digester wall.

Stainless steel tubes (parts 3) ran the length of the basket, and their purpose was to allow the insertion of thermocouples. When the basket was filled with wood chips, the thermocouples could be properly positioned by simply sliding them down the opened tube. As can be observed in the photograph, these tubes have numerous openings spaced throughout their length, and were open-ended both at the bottom and top. Hence, liquor temperature measurements were actually made in the zone of pulping.

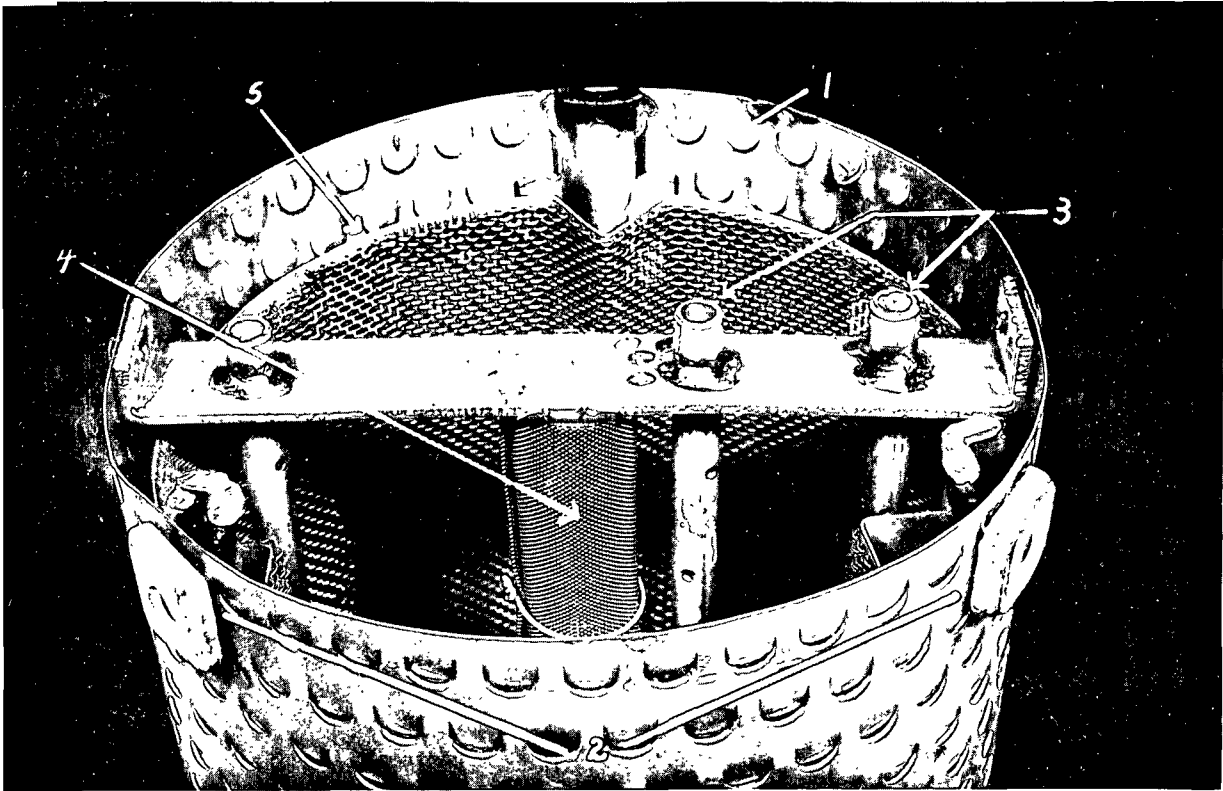


Figure 40. Chip Basket

The screened, cylindrical column (part 4) passing through the center of the basket allowed the entry of a standpipe through the bottom of the basket into the center of the chip mass. The pipe that entered this channel was appropriately drilled so that it could act as a 360° shower. The latter stage of quenching was accomplished by forcing cold water through this showerpipe, and hence outward through the chip charge.

Experimentation showed that even though the exterior basket was a good reflector, its temperature rose appreciably. To avoid transfer of heat to the wood chips, an inner basket (part 5) of stainless steel mesh was constructed. This basket was positioned away from the outer basket by transite spacers in a manner similar to that described previously. At no point did the screen basket touch the outer plate basket.

When in operation, the basket was fitted with an appropriate double lid, so as to provide the chips with complete protection. Temperature measurements throughout the basket showed that when under vacuum, the walls of Vessel No. 2 could be maintained at a temperature of 240°C. for periods as long as an hour before the temperature exceeded 50°C. in any portion of the chip charge.

APPENDIX II

TEST PROCEDURES

PULP WASHING CYCLE

The pulp removed from the digester was allowed to drain, and then was placed in 20 liters of cold water. The pulp was allowed to soak in this water for 24 hours, after which time it was passed through the Sprout-Waldron Refiner set at 0.015-inch clearance. During passage through the refiner, an additional 40 liters of cold water was added to the pulp slurry. The total slurry was then carefully dewatered on a filter, so as to avoid loss of any fines. After dewatering to a consistency of about 20%, the pulp was rediluted with fresh cold water to a volume of approximately 20 liters. This slurry was then given a second pass through the Sprout-Waldron Refiner, but with the clearance set at 0.005 inch. In a manner similar to the first passage through the refiner, 40 liters of dilution water were added to the slurry so as to obtain a final volume of 60 liters. The pulp was then dewatered a second time on a filter to a consistency of about 20%. The wet pad was then "crumbed", and the pulp stored for further testing in a polyethylene bag.

YIELD DETERMINATION

The wet crumbed pulp, after 24 hours storage, was weighed, and the moisture content was determined by sampling and drying the samples at 105°C. until constant weight was obtained. The moisture determination

was performed in triplicate, and the results averaged. The per cent yield was then calculated, based on the oven-dry weight of the wood initially charged to the digester.

BRIGHTNESS DETERMINATION

Brightness handsheets were made according to the procedures outlined in Institute Method 412 (1952) and the brightness of these specially prepared sheets was determined with the GE Brightness Meter, according to the procedures outlined in Tappi Standard T 452-m-48. The only deviation in the determination of brightness from standard procedures was in the aging of pulps. All brightness measurements were made between 56 and 58 hours after the completion of cooking. Brightness handsheets were always formed two to four hours prior to brightness measurement.

METHOXYL DETERMINATION

Methoxyl determinations were conducted according to Institute Methods 18 (1952). To avoid any interference in this test due to the presence of alcohol in the pulp, the methoxyl determination was conducted on unextracted pulp. A portion of the water-washed refined pulp was air-dried for use in the methoxyl determination.

PULP STORAGE

After about 70 hours of storage in a polyethylene bag, the wet lap pulp was broken down into approximately two equivalent portions. One portion was treated with formaldehyde (1% on the pulp basis), placed in

a polyethylene bag, and stored at a temperature of about 35°F. This formaldehyde-treated pulp was used for the determination of physical properties.

The second portion of pulp was extracted with ethyl alcohol for four hours in a Soxhlet. The extraction procedure was similar to that outlined in Institute Method 11 (1952). After extraction, the pulp was air dried and dry-fluffed in a Waring Blendor for about 30 seconds. This alcohol-dried, fluffed pulp was then stored in a polyethylene bag until such time as the chemical analysis could be performed on the material.

ETHYL ALCOHOL SOLUBILITY OF PULP

Alcohol extractives were determined on formaldehyde-treated pulp using Soxhlet extraction with 95% ethyl alcohol by procedures similar to those in Institute Method 11 (1952). All tests were performed in duplicate and the precision was within $\pm 2\%$ of the average.

PENTOSAN DETERMINATION

The pentosan content of the various alcohol-extracted pulps was determined by the bromide-bromate method, described in Institute Method 424 (1952). All determinations were run in duplicate, and the precision was within $\pm 0.6\%$ of the average.

TOTAL LIGNIN

KLASON LIGNIN

Lignin in the wood and alcohol-extracted pulp was determined in duplicate by procedures similar to Institute Methods 13 and 428 (1952), respectively. The precision was within $\pm 0.5\%$ of the average.

The Institute Method for the Klason lignin determination was modified in the following way. Fifteen minutes after the addition of 72% sulfuric acid, the test specimen was subjected to a vacuum for fifteen minutes. At the end of this period, the vacuum was released, and the samples were thoroughly stirred. The vacuum was then reapplied for an additional fifteen minutes (41). The filtration procedure used in removing the flocculated lignin was that outlined by Wise (42).

ULTRAVIOLET ABSORPTION TEST

The filtrate from the Klason lignin determination and the first amount of wash water up to one liter volume was collected, and an ultraviolet absorption run at 230 m μ . Lignin was calculated from Equation (1) with the value "a" at 230 m μ being taken as 42 according to Buchanan's ultraviolet absorption data on aspen native lignin (37).

$$\frac{C}{L} = \frac{A}{ba}$$

$\frac{C}{L}$ = conc. of lignin in g./l.

b = cell width in cm.

a = absorptivity

A = absorbance

The absorbance was determined using acid of the same concentration as a standard. All determinations were run in duplicate, and the precision was within $\pm 4\%$ of the average.

TOTAL LIGNIN

Total lignin was defined as the summation of Klason lignin plus ultraviolet lignin.

HOLOCELLULOSE PREPARATION

A chlorite holocellulose was prepared according to Institute Method 28 (1952), but with this modification; all pulp specimens were treated exactly 1/2-hour with sodium chlorite. The holocellulose preparation was then washed with hot water, cold water, alcohol and acetone. The samples were dried from acetone in an oven at 105°C. for three hours. Following weighing, a portion of the holo preparation was removed and tested for lignin content. The per cent holocellulose was determined and corrected for measured total lignin. All tests were run in duplicate, and precision was within $\pm 0.5\%$ of the average.

Viscosity or alkali-resistant cellulose measurements were not made on oven-dried material, as additional holocellulose preparations were made for these tests. Instead of drying the holocellulose material in the oven when preparing material for these tests, the holocellulose was air dried from acetone.

ALKALI-RESISTANT CELLULOSE

A sample of the air-dried holocellulose preparation was the material used for the determination of the amount of alkali-resistant cellulose. Two concentrations of sodium hydroxide, 10 and 21.5%, were used in the determination as outlined by Sutherland (43).

This method for the determination of alkali-resistant cellulose is based on volumetric procedures. A portion of holocellulose is treated with alkali of the desired concentration. The undissolved fibers are removed from the alkali slurry by filtration, washed with fresh alkali, and then treated with acid and a known excess of potassium dichromate. Similarly, the filtrate combined with the washings is treated with acid and dichromate. The amount of dichromate used in oxidation of the filtrate and residue is determined by back-titration and the percentage alkali-resistant and soluble carbohydrate calculated on the basis of the oxidation requirements.

All tests were run in duplicate, and the precision was within $\pm 0.2\%$ of the average.

VISCOSITY DETERMINATION

Cupriethylenediamine disperse viscosity of the holocellulose pulp was determined on 0.5% solutions under nitrogen according to procedures outlined by Browning, Sell, and Abel (44). All tests were performed in duplicate, and the precision was within $\pm 0.5\%$ of the average.

BEATING AND HANDSHEET FORMATION

Formaldehyde-treated, wet lap, cold storage pulp was the material used for sheet formation. The pulp was beaten in a Jokro Mill according to Institute Pulping Group Procedure 58 (1955). Handsheets were made according to procedures outlined in Institute Method 411 (1952) at five beating intervals: namely; 5, 10, 20, 30, and 40 minutes. Schopper-Riegler freeness values were determined at each beating interval according to the procedures outlined in Institute Method 414 (1952).

The eight handsheets produced at each beating interval were air dried at 50% relative humidity for a minimum of 24 hours prior to testing. The handsheets were then individually weighed to within one-thousandths of a gram. The three handsheets having the greatest deviation in basis weight from the mean were discarded and all the physical testing was performed on the remaining five sheets.

APPARENT SHEET DENSITY

Apparent sheet density was calculated from basis weight and caliper measurements according to procedures outlined by Institute Procedures 504 and 505 (1952), respectively. The unit of measurement for apparent sheet density was grams per cubic centimeter, and basis weight was reported in terms of grams per square meter.

INTERNAL TEARING RESISTANCE

Tearing resistance was determined on the Elmendorf tear tester

according to procedures outlined in TAPPI Standards T 414 m-49. Five sheets were torn simultaneously, and a total of four measurements were made. A tear factor in terms of grams of force required to tear a 100 gram per square meter basis weight sheet was calculated.

ZERO-SPAN TENSILE STRENGTH

Zero-span tensile strength was determined on handsheets from the 10-minute beating interval. The test was conducted according to procedures outlined in TAPPI Standard T 231 sm-53 and five specimens per sample were measured. The results were reported in pounds of force necessary to rupture a one-inch strip.

TENSILE STRENGTH AND STRETCH

Tensile strength and stretch were determined simultaneously on the Baldwin-Southwark Universal Tester. The specimen size was six inches by one inch, and the distance between jaws at the start of testing was three inches. In testing, the jaws moved at a constant speed of 0.15 inches per minute, and the load was measured in pounds. Five specimens per sample were tested and the tensile strength was reported in pounds per inch. The total elongation of the specimen at failure was expressed as a percentage of test length and termed "stretch".

OPACITY

The Bausch and Lomb contrast ratio was determined according to

procedures outlined in TAPPI Standard T 425 m-44. Five measurements per sample were made, and the results reported in terms of per cent of the contrast ratio

$$\text{Opacity} = \frac{R_0}{R_{0.89}} \times 100$$

RIGIDITY

The Clark rigidity factor was determined according to procedures outlined in TAPPI Standard T 451 m-45. A total of five specimens per sample were measured, and the result calculated in terms of the Clark rigidity factor.

APPENDIX III

CALCULATION OF EQUIVALENT COOKING TIME

It was desirable to correct mathematically for the small temperature variations which occurred in cooking by adjusting the cooking time to a value equivalent to a cook conducted under precisely isothermal conditions. If such a correction of the data were to be perfect with a single correction, two conditions must be met. One, a definite known relationship must exist between temperature and rate of pulping. Two, with only a single correction the reaction rate of each chemical reaction that contributes to the over-all pulping reaction must have the same temperature coefficient.

While neither of the two above stated conditions are met in the neutral sulfite pulping process, each condition is approached. As subsequent data will show, it was possible to correct cooking time for small variations in temperature (approximately 3 or 4°C.) with a considerable degree of accuracy.

To develop a relationship between the over-all pulping reaction rate and temperature, it was assumed that isothermal conditions actually did prevail during experimental cooking. A plot of the reciprocal of yield squared versus cooking time (Figure 41) showed that an approximate linear relationship existed. The general mathematical equation defining such a straight line is expressed by:

$$\frac{1}{Y^2} = kt' + B \quad (1)$$

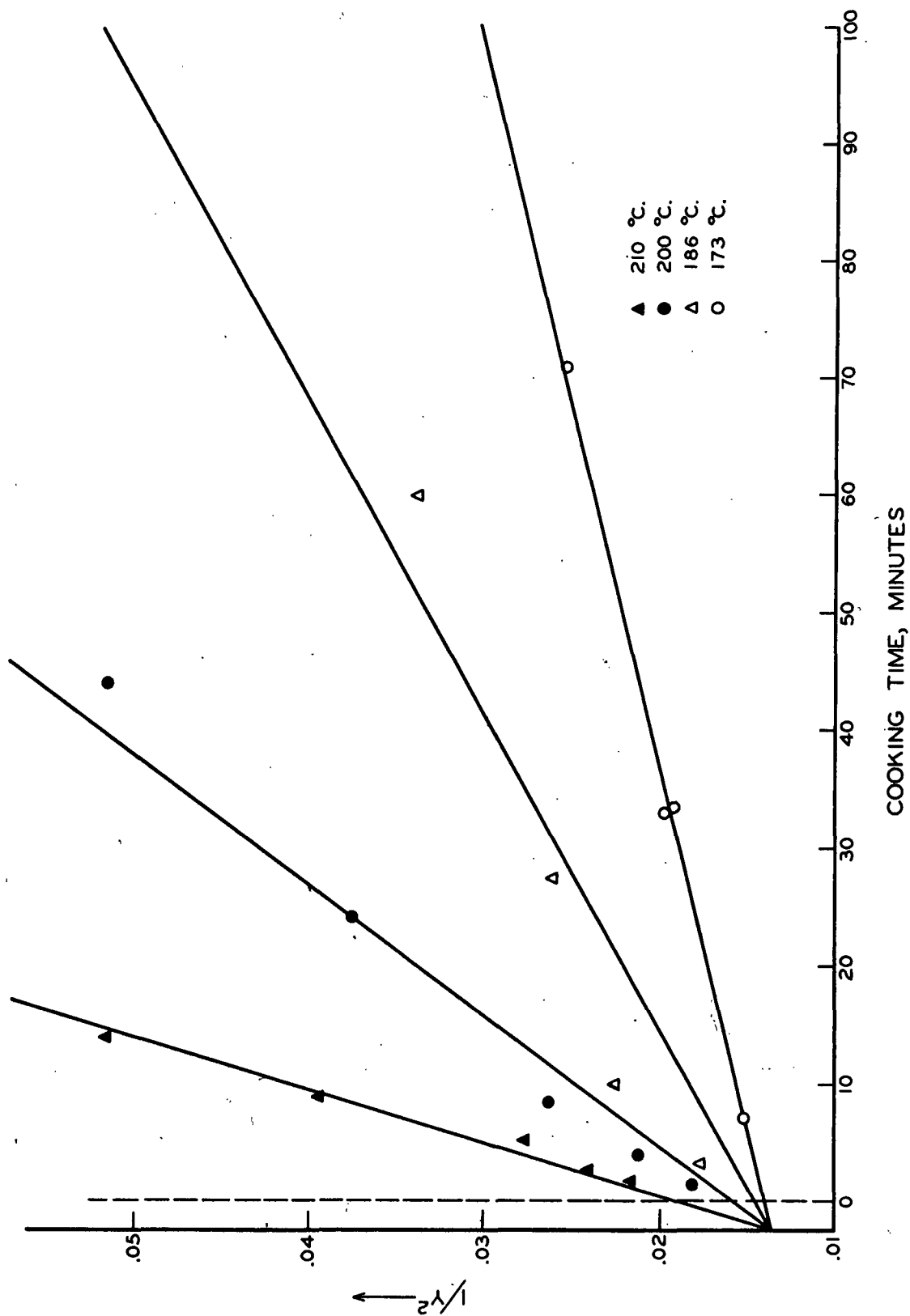


Figure 41. Reciprocal of Yield Squared vs. Cooking Time

where \underline{k} equals the proportionality factor relating yield (\underline{Y}) and time ($\underline{t'}$). The values of \underline{k} and \underline{B} were determined from the graph by means of the method of averaging.

The values of $\log \underline{k}$ so obtained minus a constant plotted against the reciprocal of the absolute temperature rectified the data, and this plot can be found in Figure 42. The equation of the line was calculated by the method of averages and was found to be:

$$\log (\underline{k} - .000067) = 14.2148 - \frac{8158.1}{\underline{T}} \quad (2)$$

The isotherms relating yield and time in Figure 41 do not pass through the origin. Hence, the location of an isotherm is dependent on slope (\underline{k}) and the \underline{Y} -axis intercept (\underline{B}). Obviously, both of these variables are temperature-dependent.

For simplicity in calculation, it was desirable to relate all temperature effects to only one variable. This could be done by observing that all the isotherms pass through a common point, \underline{P} . Therefore, Equation (1) could be mathematically corrected to create a shift in origin so that point \underline{P} , (2.5, 0.014), would coincide with the origin. Equation (1) then became

$$\left(\frac{1}{\underline{Y}} - 0.014\right) = \underline{k}(\underline{t'} + 2.5) \quad (3)$$

and this equation related yield and time through the single variable, \underline{k} .

Equation (3) was derived with time being measured in minutes. For the calculation of equivalent cooking time, it was more desirable to express

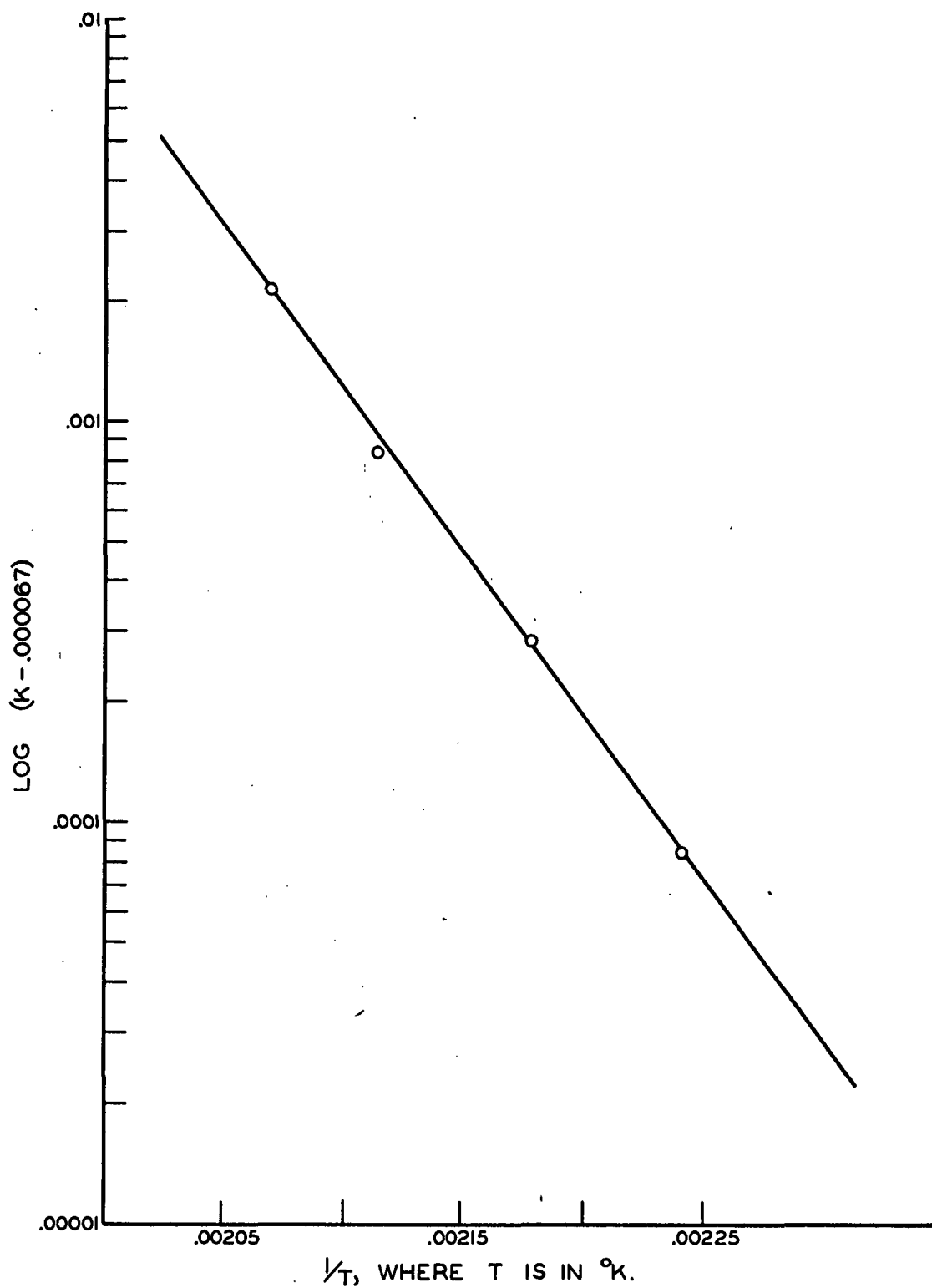


Figure 42. Log Proportionality Factor (Relating Time and Yield) vs. Reciprocal Absolute Temperature

time in seconds. To accomplish this, Equation (3) need only be multiplied by 60. Equation (4) represents an expression equivalent to Equation (3) except that time is measured in seconds and the term \underline{Z} has been substituted for 60 ($\frac{1}{2} - 0.014$).

$$\underline{Z} = \underline{k}(\underline{t} + 150) \quad (4)$$

To check the accuracy of Equation (4), the " \underline{Z} factor" was calculated for each cook, again assuming that isothermal experimental conditions did exist. These calculations (Figure 43) predicted pulp yield within $\pm 3\%$. With Equation (4) holding true over such a wide temperature range, it was felt that the \underline{Z} factor could be used with considerable accuracy for small temperature changes.

To correct the over-all cooking time for minor temperature variations, the following procedure was adopted. The cook was divided into 10-second intervals and the average temperature of each interval determined. The delta \underline{Z} ($\underline{Z} = \frac{\Delta}{k} \underline{k} \underline{t}$) for each interval was then calculated from the differential form of Equation (4). The summation of delta \underline{Z} 's was then obtained and converted to an equivalent cooking time through division by the reaction rate, \underline{k} . An example of this calculation for equivalent cooking time can be found on the following page.

A similar treatment was made by Vroom (46).

SAMPLE CALCULATION, EQUIVALENT COOKING TIME

Cook 34

Temperature, °C.	No. of 10-Sec. Intervals at Temp.	$\underline{K} \times 10^{-4}$	$\frac{K\Delta t}{\text{delta } \underline{Z}}$
180	1	2.27	.000227
182	1	2.59	.000259
183	1	2.78	.000278
184	3	2.98	.000894
185	10	3.20	.003200
186	<u>3</u>	3.43	<u>.001029</u>
Total	19	$\Sigma \Delta \underline{Z} =$.005887

$$\text{Equivalent Cooking Time} = \frac{\Sigma \Delta \underline{Z}}{\underline{K}_{(186)}} = \frac{.005887}{.000343} = 172 \text{ seconds}$$

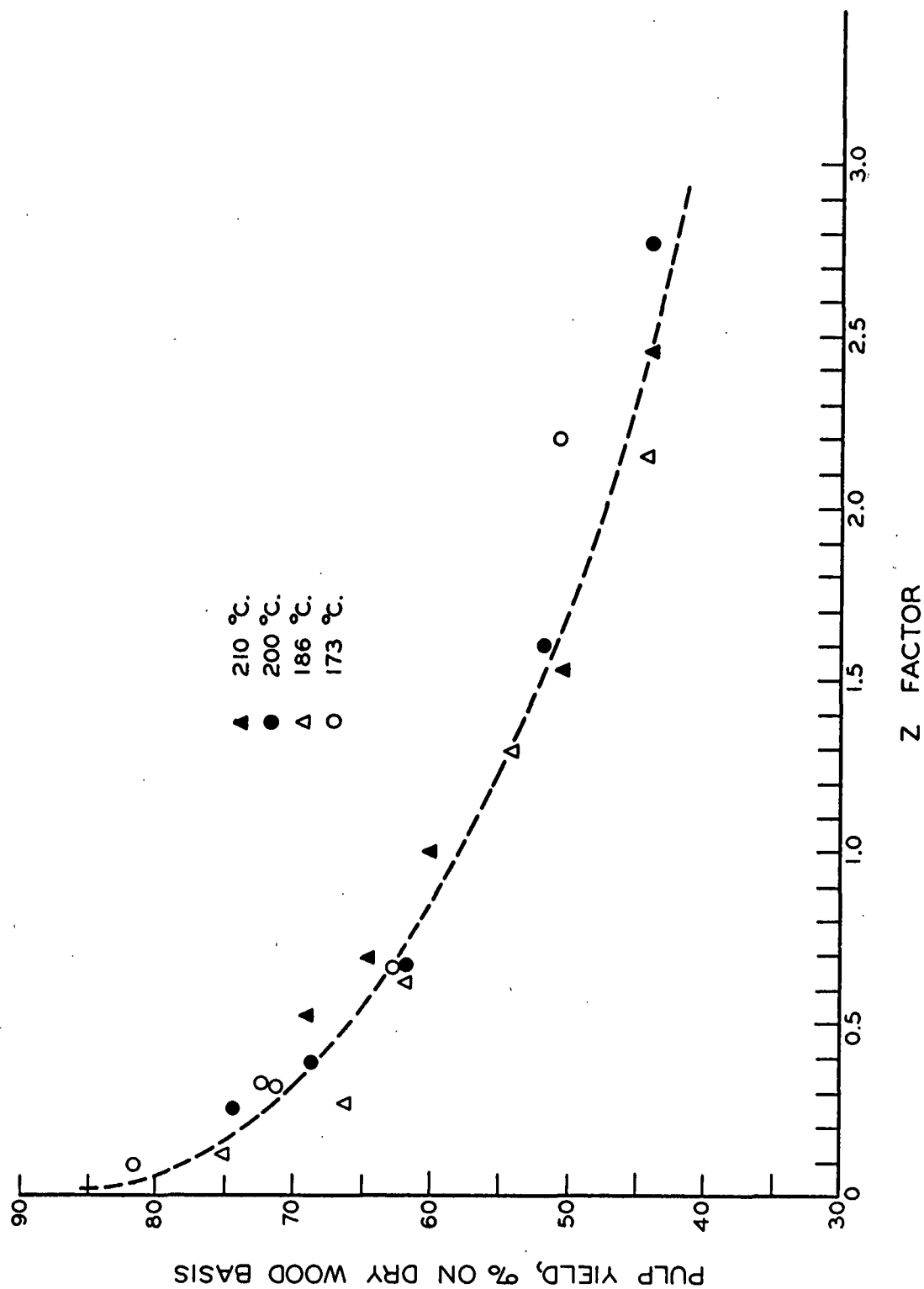


Figure 43. Pulp Yield vs. Z Factor

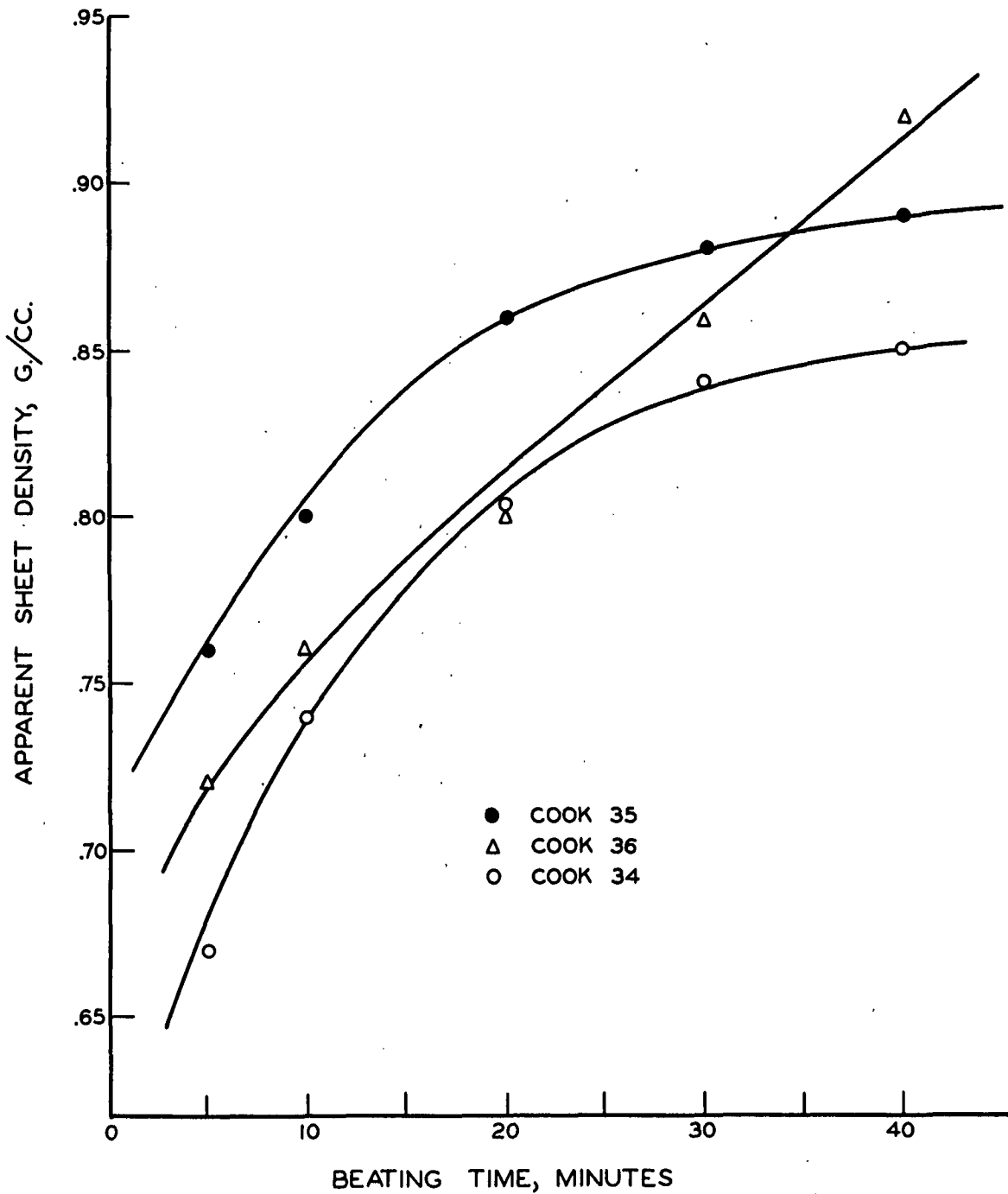


Figure 44. Apparent Sheet Density vs. Beating Time (Pulping Temperature = 186°)

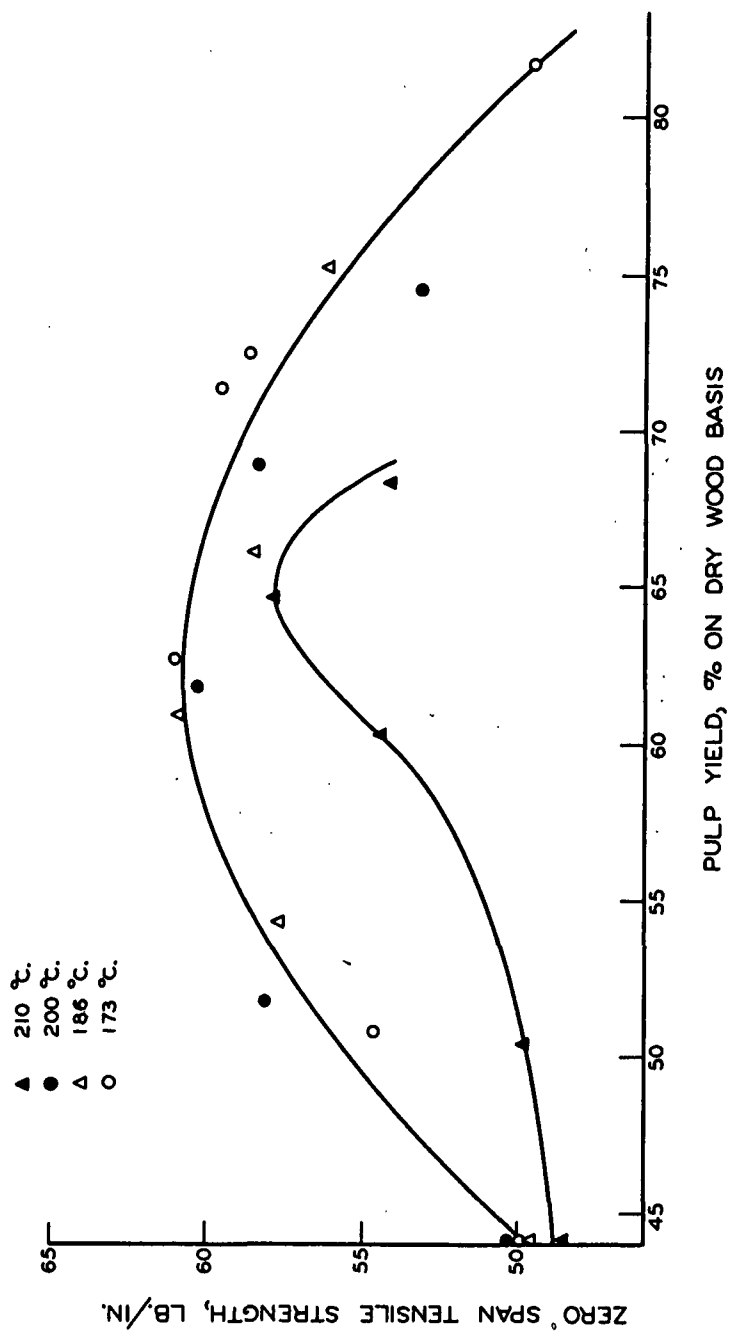


Figure 45. Zero-Span Tensile Strength vs. Pulp Yield

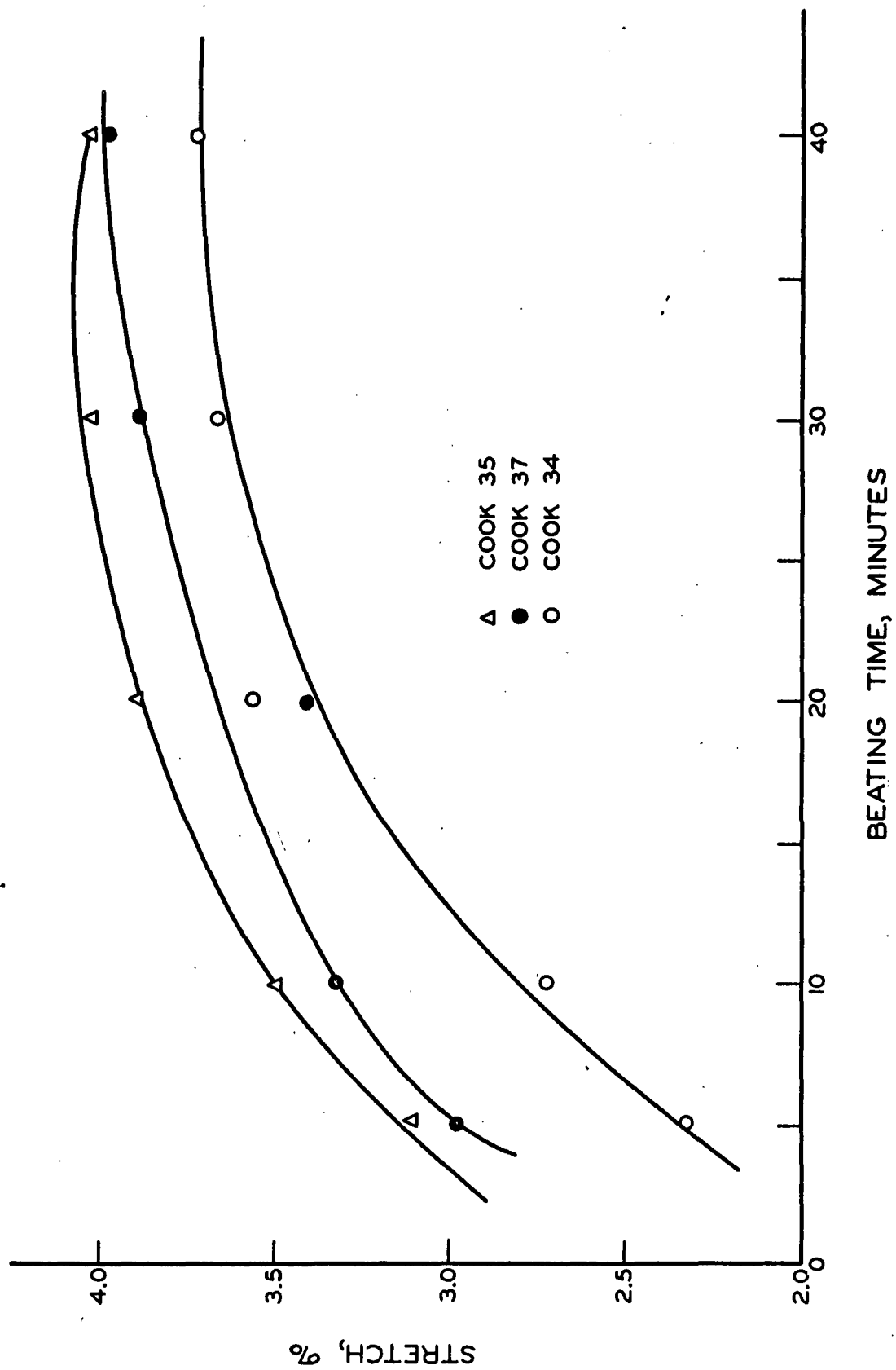


Figure 46. Stretch vs. Beating Time (Pulping Temperature = 186°)

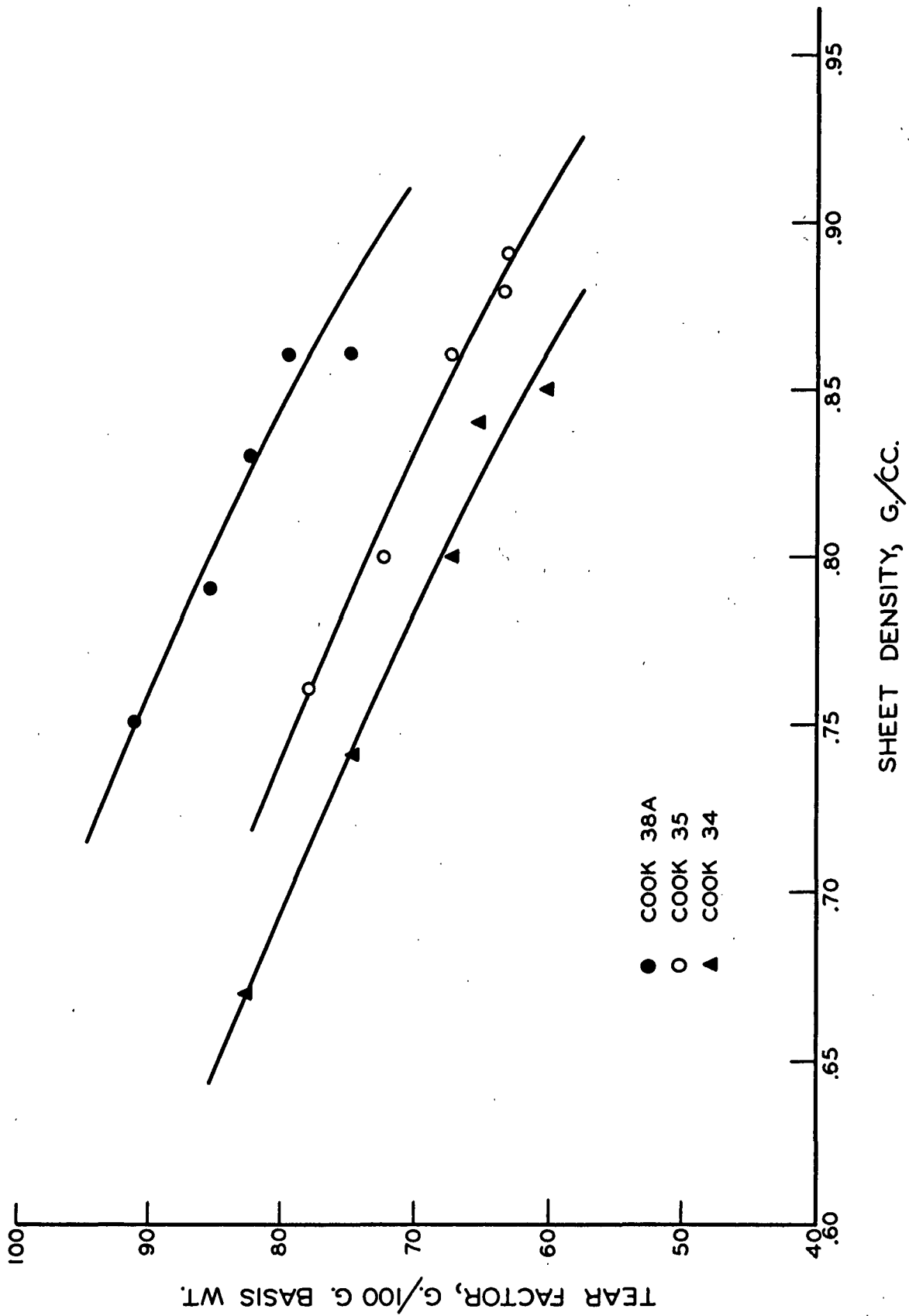


Figure 47. Tear Factor vs. Apparent Sheet Density (Pulping Temperature = 186°)

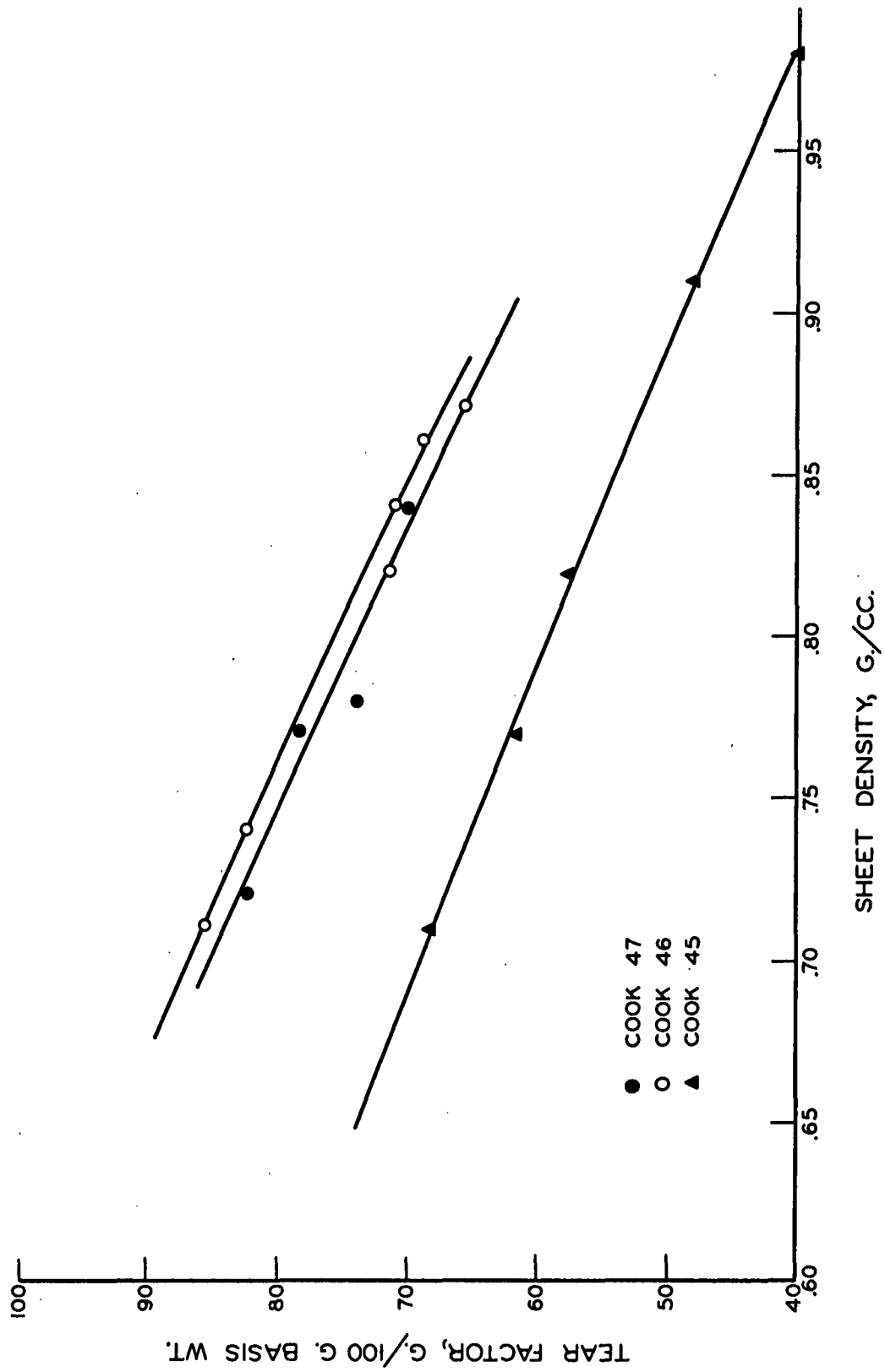


Figure 48. Tear Factor vs. Apparent Sheet Density (Pulping Temperature = 210°)

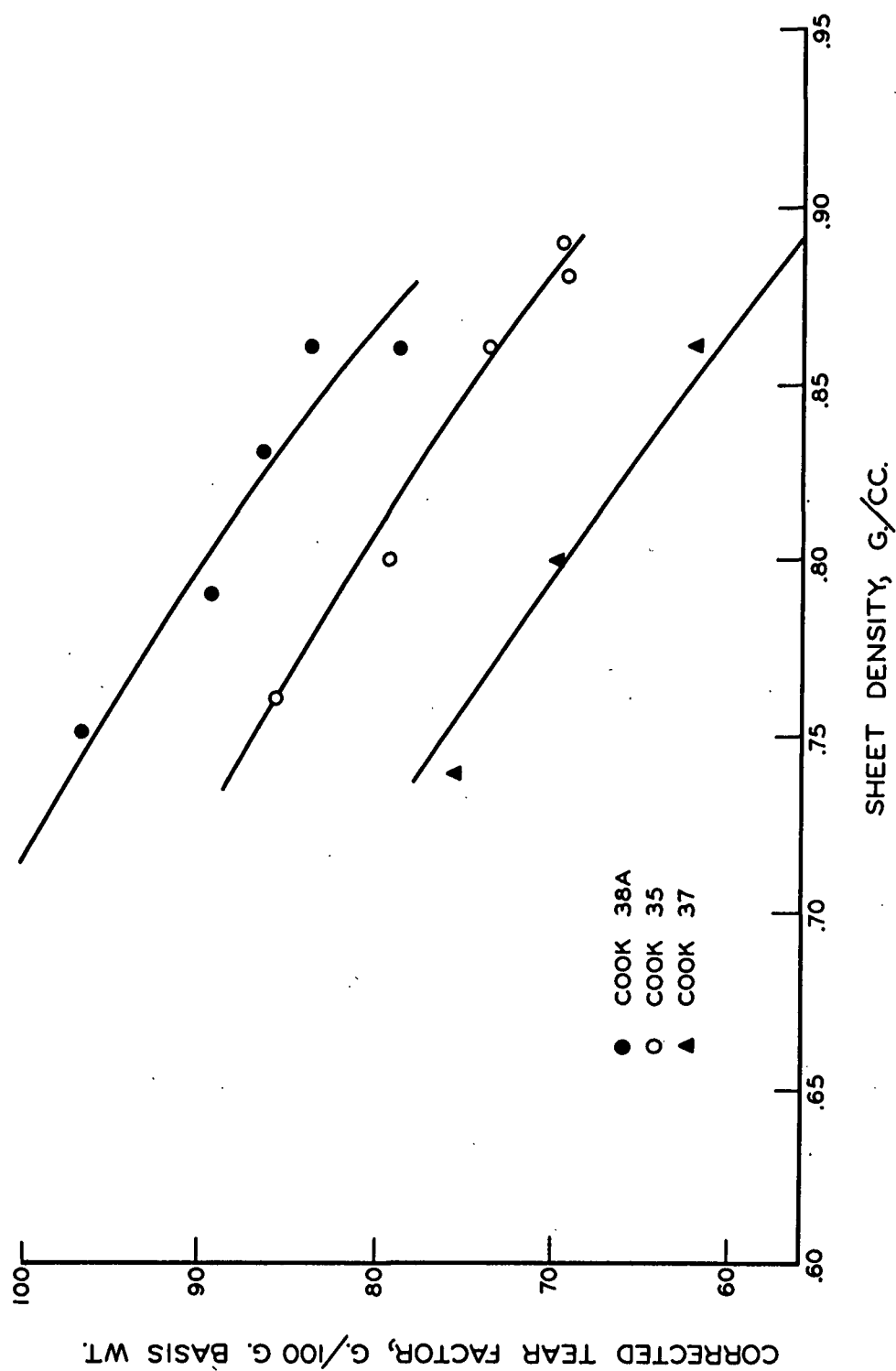


Figure 49. Corrected Tear Factor vs. Apparent Sheet Density (Pulping Temperature = 186°)

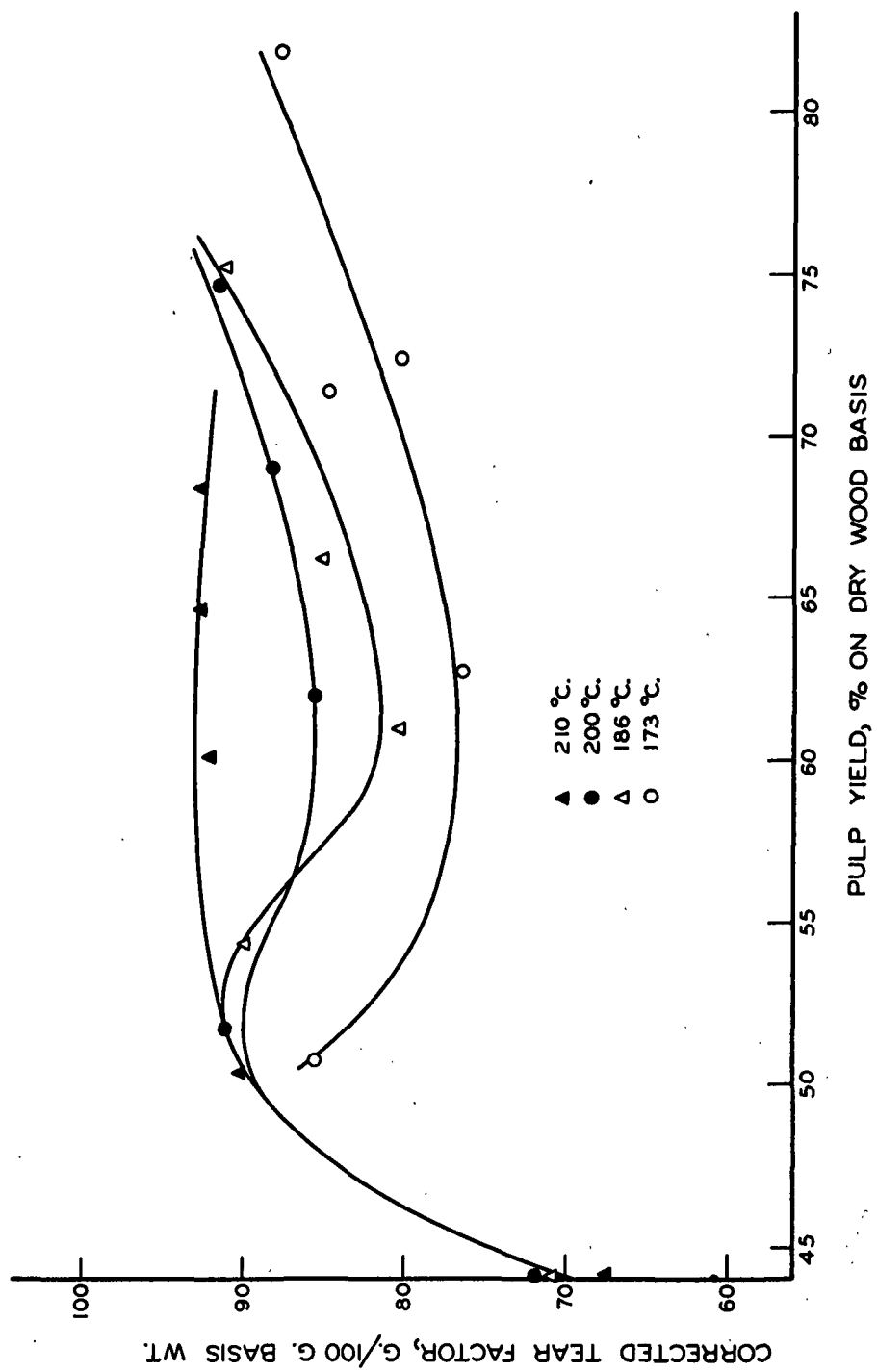


Figure 50. Corrected Tear Factor vs. Pulp Yield (10-Min. Beating Time)

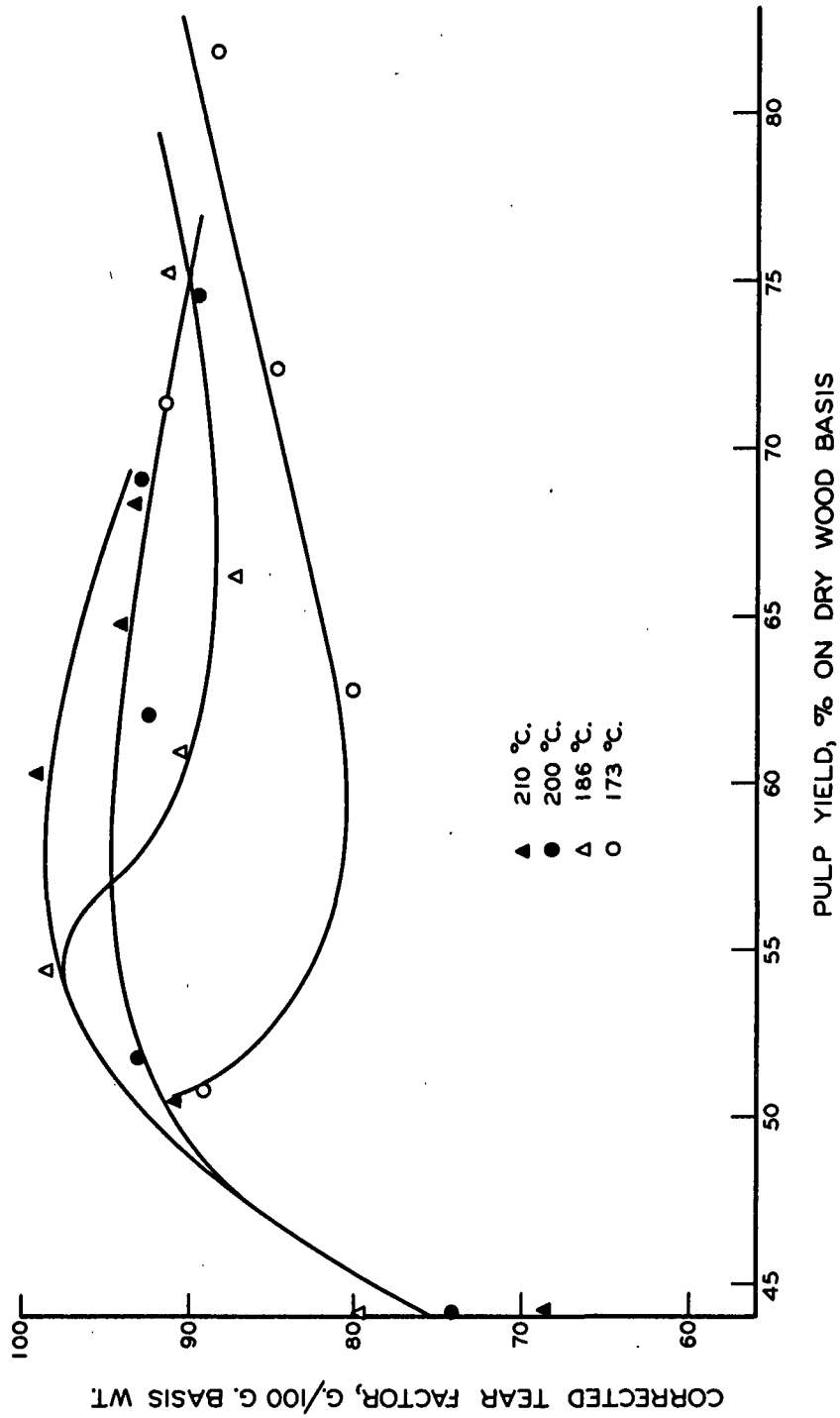


Figure 51. Corrected Tear Factor vs. Pulp Yield (.73 = Sheet Density)

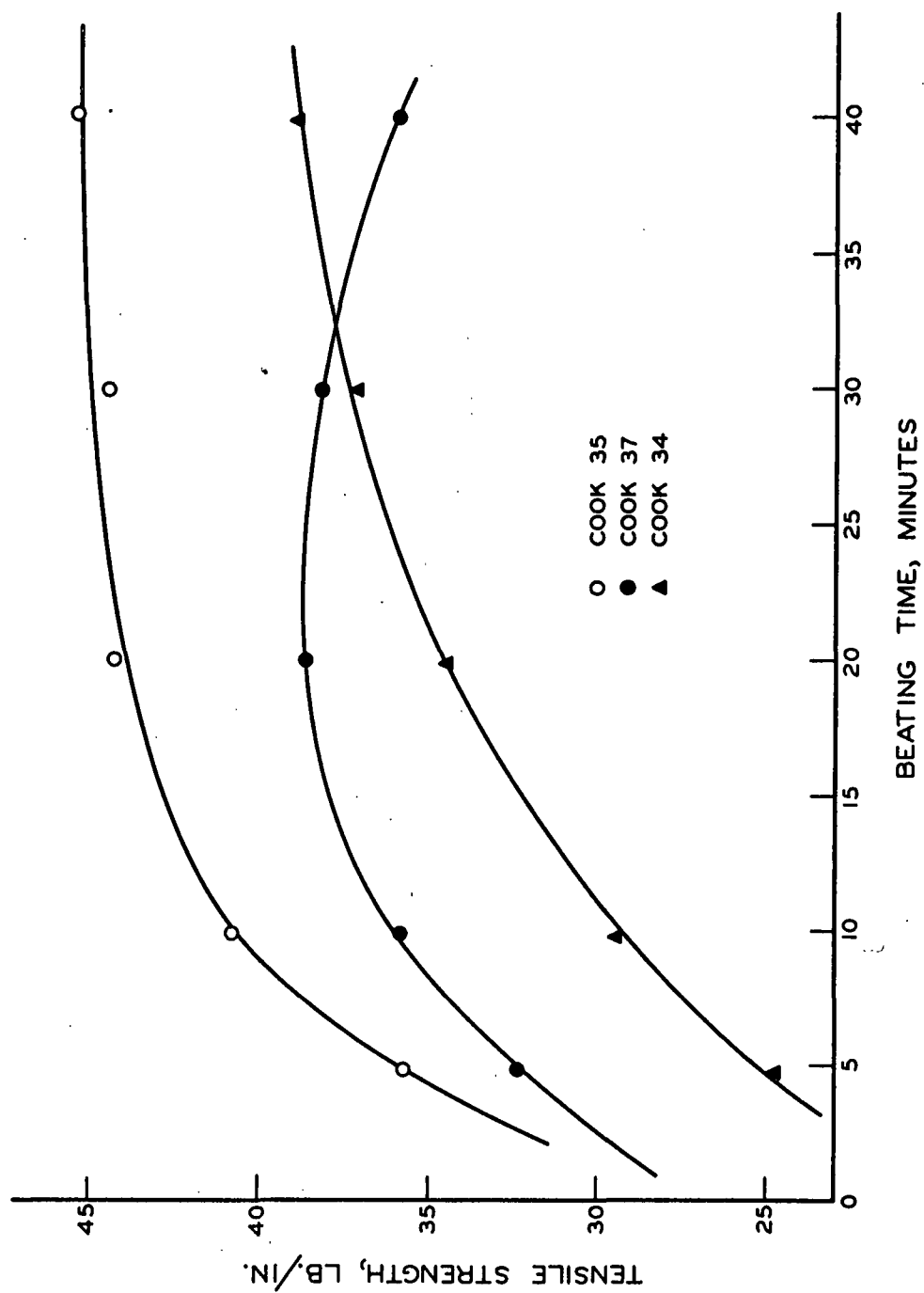


Figure 52. Tensile Strength vs. Beating Time (Pulping Temperature = 185°)

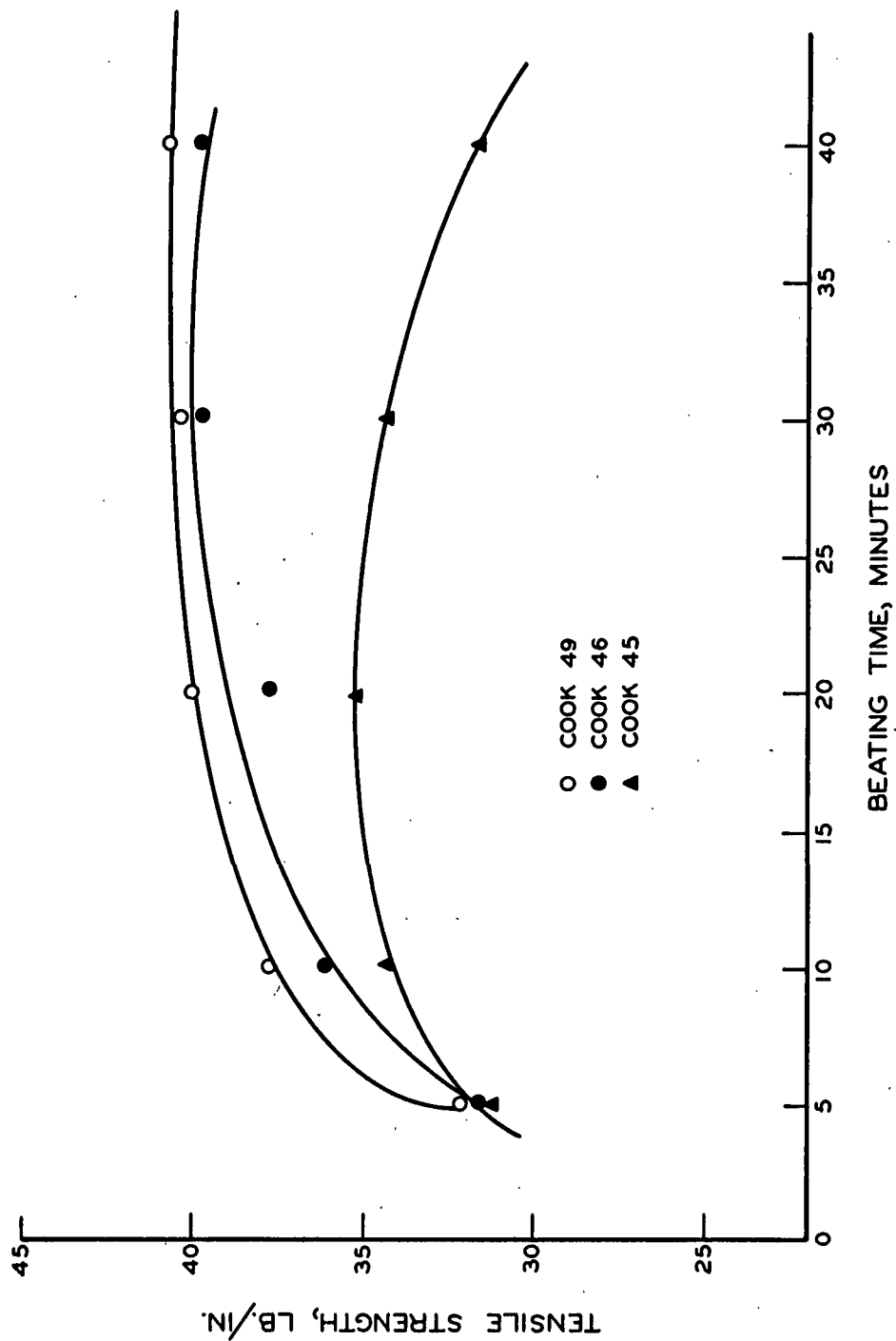


Figure 53. Tensile Strength vs. Beating Time (Pulping Temperature = 210°)

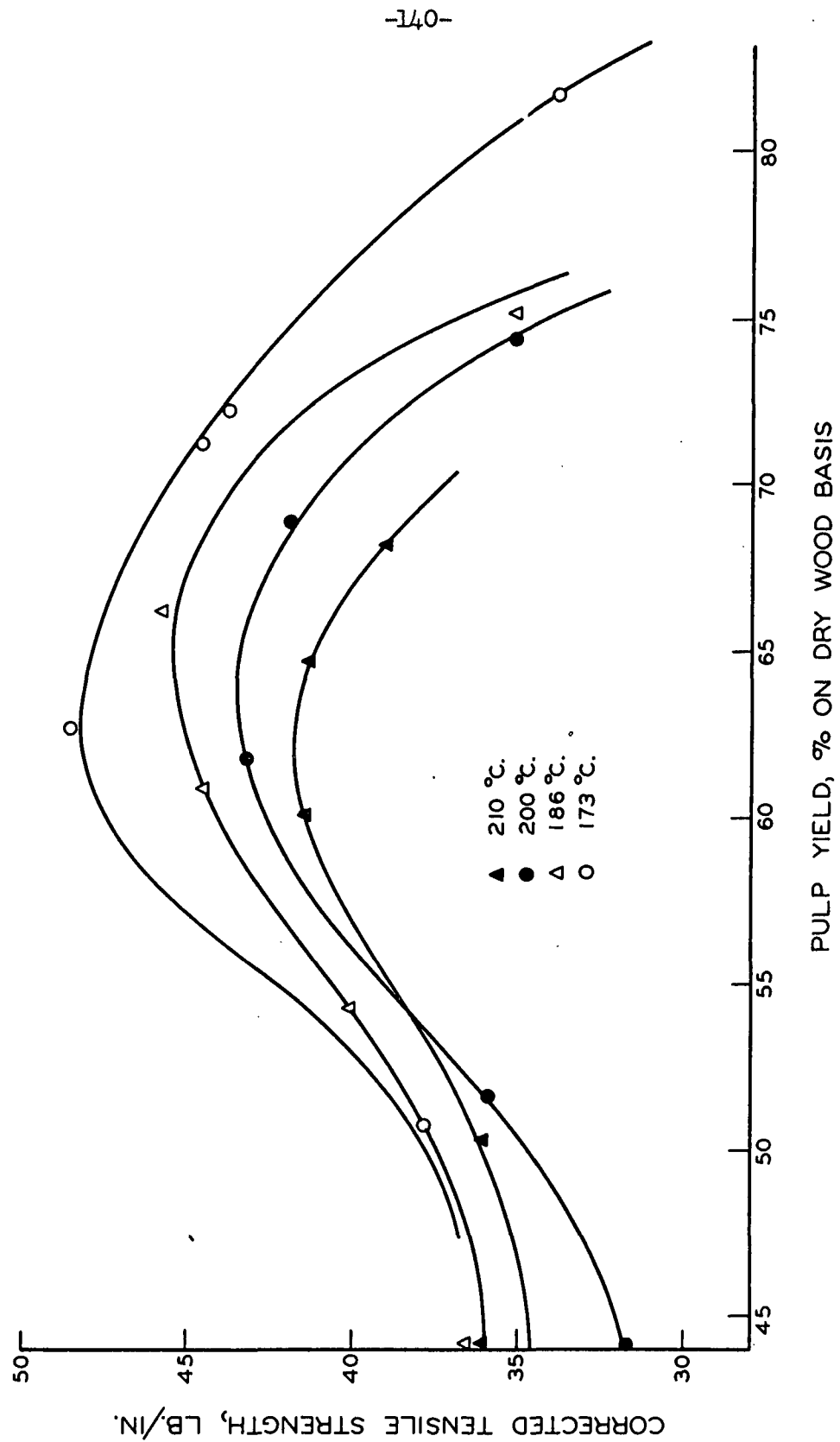


Figure 54. Corrected Tensile Strength vs. Pulp Yield (10-Min. Beating Time)