PENETRATION
IN
SULPHITE COOKING

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PENETRATION IN SULPHITE COOKING

A Thesis

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M.

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INTRODUCTION

The present investigation deals with the study of the variable conditions - temperature, pressure, concentrations, catalysts, duration of reaction, structure of wood, etc. - which influence the course of the sulphite process for the manufacture of paper pulp from wood. Under mechanical conditions is included pre-treatment of the wood with a view to bringing about controlled conditions of penetration of the cooking reagents into the wood. This latter has to do not only with the shape and size of the wood chips but also with the means of bringing the reactants into intimate contact and ensuring that this intimate contact prevails during the course of the cooking process.

An enormous number of investigations has been carried out in the past on the sulphite cooking process, the results of which are recorded in the literature. Still more information has been stored up in the archives of private firms, much of which is based on long practical experience rather than on strictly experimental evidence. Part of this has leaked out in the form of what might be called commonly accepted knowledge, which is frequently rather indefinite, and the truth of which it is often difficult to confirm. Thus, an investigator in this field is faced with the double difficulty of avoiding duplication of results and, at the same time, of guarding against forming preconceived ideas based on information which may be erroneous. Among the most important investigations mentioned in the literature are the systematic researches which have been conducted at the Forest Products Laboratories at Madison, Wisconsin, under the direction of Miller and Swanson, and the extensive work on the chemistry of the sulphite process carried out by Hägglund and his co-workers at the Cellulose-Technique and Wood-Chemistry Institute in Stockholm.

This thesis has been written on the presumption that the reader is, to some extent, familiar with the general principles of the sulphite pulping process. A detailed description of the process and of its various modifications would be far too lengthy; consequently, only the broad lines involved will be outlined here. For greater detail, the reader is referred to the standard texts on pulp and paper technology[1,2] or, for a briefer account, to the recent excellent article of Davies[3].

Wood, usually spruce, in the form of chips about 3/4" long, is charged into large steel digesters lined with acid-resisting brick. The cooking liquor consists of an aqueous solution of about 1% lime and about 5% sulphur dioxide; the sulphur dioxide is, therefore, present partly as free sulphurous acid and partly combined as calcium bisulphite. Liquors containing magnesia instead of lime as the base, or mixtures of magnesia and lime are also used. This liquor is run into the digester until it covers the chips. On this continent, the "quick-cook" or "direct steam" process is used almost exclusively. Here, the digester contents are heated by forcing steam directly into them from jets near the bottom of the digester, the steam also serving to circulate the liquid. Temperature schedules vary considerably from mill to mill. The temperature may be raised more or less rapidly to about 100°C. but it is always controlled so as to never exceed 110°C. for at least two hours and usually for an appreciably longer time. Unless this is done, the centres of the chips are found to be hard and brown. After the period below 110°C., the temperature is raised gradually to a maximum between 140 and 150°C., the pressure being maintained at a maximum of from 75 to 90 pounds per square inch by allowing the escape of gases and liquid, i.e. "relieving" the digester. The total cooking time may vary from eight to sixteen hours. Shortly before the end of the cook, the pressure is lowered to about 45 pounds per square inch, and the digester contents blown from a valve at the bottom of the digester into a large pit where the chips disintegrate and the pulp is washed and collected.

Important improvements have been made in the process in recent years, such as the development of the "Chemi-pulp" process involving the use of preheated cooking liquor and much more efficient heat recovery. Mechanical circulation of the cooking liquor by auxiliary pumps is also coming into widespread use, resulting in more uniform cooking and improved pulp quality.

It may be useful at this time to discuss in some detail the significance of the term "penetration" as used in this thesis. The entrance of a dissolved substance into a porous solid such as wood may take place in two ways. Firstly, by "natural penetration", this term describing the entrance of a dissolved reagent into a portion of solid, already filled by the solvent, and surrounded an all sides by the solution of the reagent concerned. This term is, therefore, synonymous with diffusion. Consequently, natural penetration will be governed by osmotic pressure differential, and independent of hydrostatic pressure differential.

All other modes of entrance of a solute into a solid are included in the term "forced penetration", and have as a common and distinguishing characteristic the mass motion of solution caused by hydrostatic pressure differential. The presence of a gaseous phase within the solid is also frequently involved. This term will, therefore, cover the case of a portion of porous solid, either filled with gas or evacuated, surrounded on all sides by a solution to which artificial hydrostatic pressure may or may not be applied. It will cover also the special case where a solution is forced completely through a section of solid by the creation of a hydrostatic pressure differential between the two sides of the solid section. In the latter case, liquid flow may be continued indefinitely as long as the pressure differential is maintained.

Except in a few instances, "forced penetration" is involved in the work presented in this thesis.

The present investigation was carried out from the point of view of the physical chemist. Because of the nature of the problem, the early fundamental research on the sulphite cooking process is due to the organic chemist, and the knowledge accumulated by him is, of course, extensively used in the present research. Approaching the problem from the physico-chemical standpoint, the first prerequisite was to establish reproducible experimental conditions. Starting with a raw material, wood, which is widely variable meant working on the smallest scale practicable, so that specimens as homogeneous as possible could be used. Considerable precautions were taken to ensure accurate control of the temperature, pressure, concentrations, etc., the important point being that one of these factors, each of which influences the results, could be varied at will with the certainty that the others were constant. Apparatus and experimental technique to meet this requirement have been developed and constitute the justification for undertaking the work. As will be seen later, the small scale technique was followed, where desirable, by experiments on successively increasing scales to ascertain the influence of uncontrollable variations in the homogeneity of the raw material.

The greatest emphasis of all, from the point of view of novelty of experimental technique, must be laid on the attempt to control the impregnation of the wood with the cooking reagents. Such an attempt has been made possible because of information obtained in this laboratory on the penetration of liquids into wood. The influence of wood structure, temperature, pressure differential, adsorption (differential adsorption in the case of sulphite liquor) have all been thoroughly investigated already. One of the objectives, when the present research was initiated, was the amplification of the penetration work dealing with the important part played by a discontinuous phase in hindering penetration, and the particular contribution to this work made by the writer will be found in the beginning of the work described. It will be seen, in this connection, that the influence of a non-condensible gaseous phase on penetration was of paramount importance in determining the course of the subsequent investigation.

Apart from its application to experimental procedure, the physico-chemical attitude also governed the direction of the research and the interpretation of results. Where possible, a number of mechanisms for various stages of the cooking process were considered and the conclusions arrived at were obtained by a process of elimination. Thus, the removal of all but traces of air from the cooking system was shown to be of influence from a mechanical and not from a chemical point of view. The "burning" of chips was examined to determine whether it was due to the presence of acid produced by oxidation or by reaction, or due to some other cause. The necessity of holding the cook below a "critical temperature" of 110°C. for varying lengths of time to avoid burning was investigated to see whether there was involved a slow preliminary chemical reaction which had to be allowed to come to completion before subsequent rise in temperature, or whether the problem was one of imperfect penetration. It can be stated that some of these questions have been answered in a positive manner; they are mentioned here to serve as examples of the objectives of the research to be described.

The physico-chemical viewpoint adopted in this research has been strongly stressed. The writer is anxious that this be not construed as implying a belief in the superiority of this type of attack as compared to investigation strictly along the lines of organic chemistry. Far from this, the writer is convinced of the indispensability of both lines of approach to a problem of this complicated nature, and firmly believes that even closer co-operation between the physical and the organic chemist than exists at present would greatly accelerate the solution of the numerous problems which confront the sulphite technician.

As mentioned before, the amount of work on these problems reported in the literature is very large. Interpretation and correlation of the results is made very difficult and confusing by the flagrant contradictions offered by much of the experimental evidence and conclusions presented. Therefore, it is impossible to give any comprehensive review of the literature in a dissertation of this size. An attempt at abbreviation, it is feared, would result only in an assembly of isolated findings which could be but of little use to the reader. Consequently, the writer has deemed it wiser to give a résumé of the work carried out in this laboratory which led to the present investigation, and to disseminate throughout the body of the thesis such references to the literature as relate directly to specific phases of the work.

What is written above may be looked upon as an attempt to imbue the reader with a general impression of the nature of the problem and with the "leit motif" of the investigation . A short review of the work carried out in this laboratory will further this.

In 1927, Dr. John Campbell (of the International Paper Company) suggested to the Pulp and Paper Division of the Forest Products Laboratories of Canada the desirability of an accurate and systematic study of the penetration of liquids into wood. This suggestion was incorporated into the research program of the Laboratories, and between 1927 and 1929, Dr. H. W. Johnston[4], under the direction of Dr. O. Maass, made a preliminary investigation of the penetration of liquids into jack pine. Beginning in 1930, this work has been continued and developed by graduate students in Physical Chemistry at McGill University.

Dr. J.W.Sutherland[5] studied the penetration of water into various species of wood. He found that penetration takes place almost entirely longitudinally, i.e. along the fibre direction, in the case of acidic solutions, and that sapwood is far more permeable than heartwood from the same tree. The rate of loggitudinal pemetration increases with decrease in the thickness of the specimen, a great increase in rate being observed when the thickness becomes less than one fibre length. The rate of penetration increases in slightly more than proportional manner with increase in pressure differential, irrespective of the absolute values of the driving and back pressures. Also the penetrability is not permanently altered by application of pressure. The rate of penetration was found to increase with temperature, and that heating to above 70°C. produced a permanent increase in the permeability at room temperatures. Sutherland also found that gases penetrated seasoned wood easily, but that wet heartwood strongly resisted penetration by gases . From his evidence, Sutherland concluded that there is no valve action on the part of the pit membrane tori of the tracheids.

Simultaneously, Dr. H.H. Saunderson[6,7] studied the penetration problem from the point of view of those peculiarities offered by sulphite liquor. He found the rate of penetration to increase with concentration of free sulphur dioxide, this increase becoming more noticeable at higher temperatures. He showed conclusively that the precipitate thrown down from sulphite liquor at higher temperatures was calcium monosulphite, and that this precipitate seriously hindered penetration into open-grained wood, the effect being purely a mechanical plugging action. With very dense wood, the effect of the precipitate was negligible, the openings in the pit membranes continuing as the limiting factor in governing the rate of flow. Saunderson found that delignification of wood with sulphite liquor proceeded more rapidly when a continuous flow of liquor was passing through the wood. He showed that, at high temperatures, the free sulphur dioxide penetrated wood much more rapidly than the combined sulphur dioxide, but that in the presence of a sufficient supply of both lime and sulphur dioxide wood may be heated rapidly to 140°C. without burning occurring. Sorption experiments showed that the sorption of free sulphur dioxide was about four times as great as that of combined sulphur dioxide, and that, as with true adsorption, the temperature coefficient was negative. Investigation of the time taken by chips to sink in sulphite liquor showed that the presence of air in the wood is the most serious hindrance to penetration, and that its removal by evacuation greatly reduced the time required for sinkage.

The present investigation was undertaken as a continuation of the work of Dr. Saunderson. Early results indicated the desirability of applying the findings to the cooking process, and to the possibility of an advantageous modification of the existing process as carried out industrially. Thus, much of the work presented deals with the development of a pre-treatment procedure based on the knowledge of penetration previously acquired. This also supplied data permitting a better understanding of the phenomenon of the "burnt cook". Since the properties of the pulps obtained by the modified process appeared abnormal, the investigation was extended to include the study of those factors which might influence the course of the process and the properties of the resulting pulps, although still keeping in mind the penetration aspect of the problem.

A systematic study of the sulphite process should take into account the following factors:

1. Species of wood
2. Wood density and structure
3. Moisture content of the wood
4. Chip size and shape
5. Temperature schedule
6. Liquor composition
7. Ratio of liquor to wood
8. Maximum pressure maintained
9. Methods of relief
10. Pre-treatment of the wood

The aim of the investigation has been to touch on as many of these factors as possible and to give more extensive study to those which appeared of greater importance. It should be reiterated that although many of these factors have already been investigated, the work has never before been carried out in a small scale apparatus which permitted such accurate and independent control of the variables involved.

It may not be amiss to comment briefly on the range of experimental conditions covered. There has been a tendency in the past, unfortunate in the writer's opinion, to limit laboratory investigations on sulphite cooking to the range of conditions found in industrial practice. This range is necessarily restricted, by economic considerations on the one hand and by limitations of existing equipment on the other. It appears only logical that the use of a wider range of conditions will at least supply more ample data and possibly reveal phenomena which may not be evident in a more narrow range. With this in mind, the writer has frequently used experimental conditions deliberately which could not be employed, at least at present, on a commercial scale.

In the following pages will be found a description of the apparatus and of the experimental procedure used. This is followed by the experimental results obtained. The headings under which these experimental results fall will be found itemized in the table of contents at the beginning of the thesis. With the results have been included brief discussions of these results, together with references to comparable work done by other investigators. The thesis is terminated by a general discussion of the results and by the conclusions drawn from them.

APPARATUS

The penetration apparatus

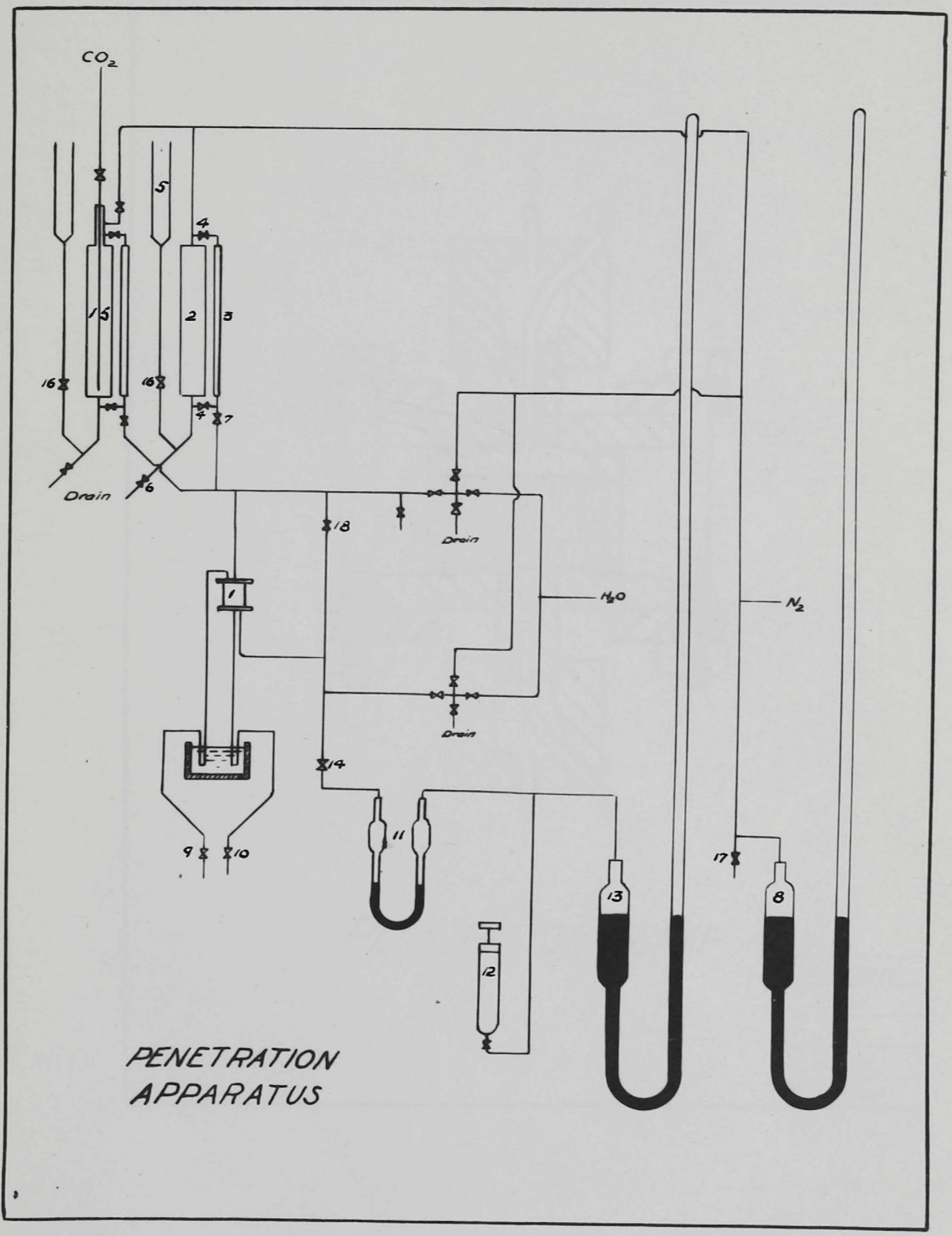
A diagram of the complete penetration apparatus is given in Figure 1. Since the complete apparatus was used for only a very few of the runs reported in this thesis, it would be superfluous to give a detailed description. The following description has been confined to a list of the component parts, numbered as in Figure 1. and it is hoped that,with this supplement, the diagram will be self-explanatory. The essential parts are:-

(a) The clamp (1) for holding the wood during a run. The details of the construction of this clamp are shown in Figure 2.

(b) The front pressure system which contains and controls the liquid to be forced through the wood. This consists of:-

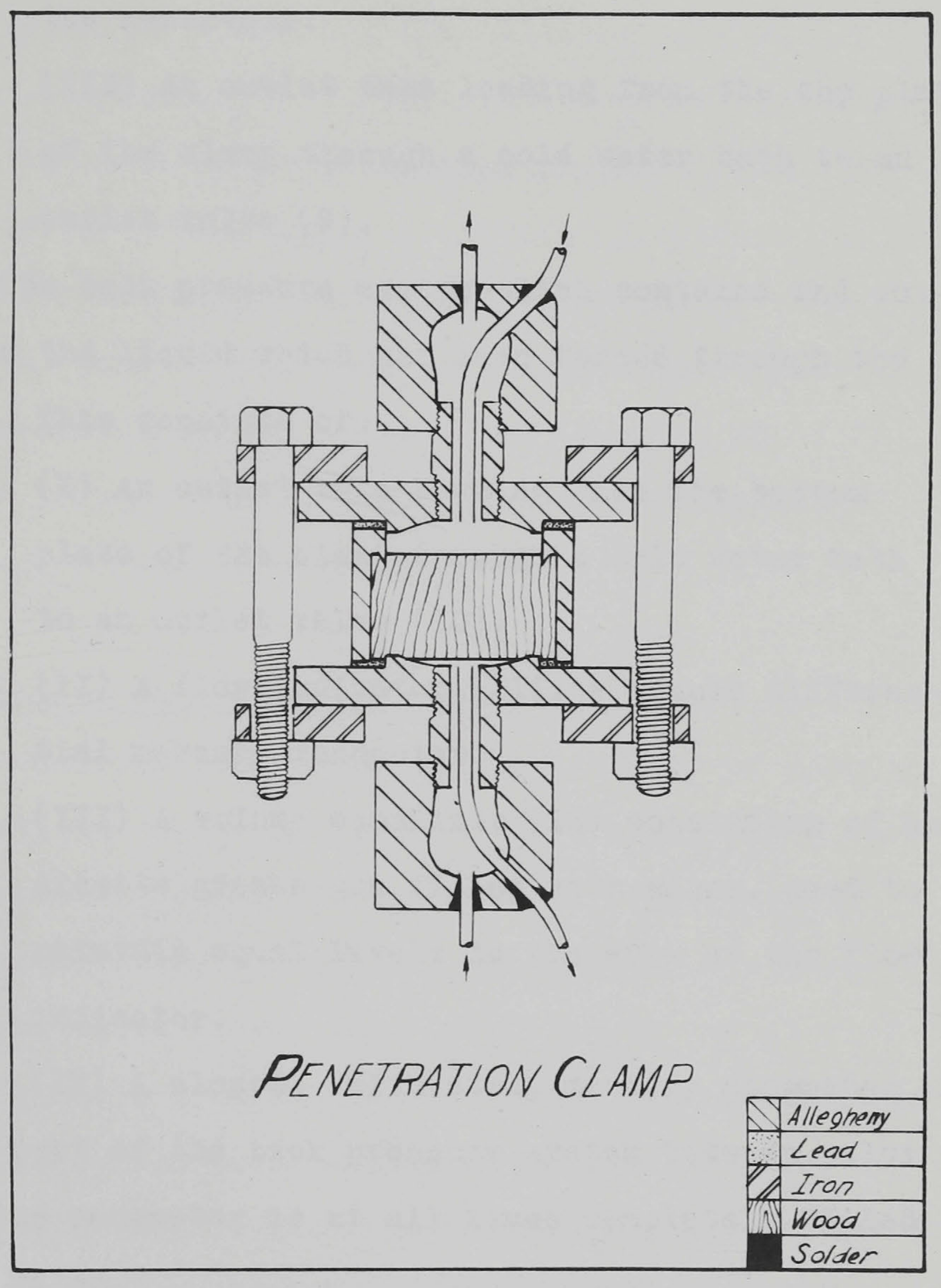
(I) A brass cylindrical reservoir (2) and gauge tube (3) connected by brass water gauge valves (4) fitted with a glass funnel (5) to permit filling by gravity and with a drainage valve (6). The top of the reservoir is connected to a nitrogen cylinder through a reducing valve and the bottom of the gauge tube to the clamp through a needle valve (7).

Figure 1.



PENETRATION
APPARATUS

Figure 2.



(II) A closed, calibrated mercury manometer (8) connected to the nitrogen tank in parallel with the reservoir.

(III) An outlet tube leading from the top plate of the clamp through a cold water bath to an outlet valve (9).

(c) The back pressure system which contains and controls the liquid which has been forced through the wood. This consists of:-

(I) An outlet tube leading from the bottom plate of the clamp through a cold water bath to an outlet valve (10).

(II) A flow indicator (11), a simple differential mercury manometer.

(III) A volume equalizer (12) consisting of an Alemite grease gun filled with water, used to maintain equal levels in the arms of the flow indicator.

(IV) A closed, calibrated, mercury manometer (13). That part of the back pressure system between valve (14) and the manometer is at all times completely filled with water.

(d) A constant temperature bath. This will be described with the simplified cooking set-up.

The chief modification made in the original penetration apparatus[6] developed in this laboratory and described above was the addition of a second liquid reservoir (15). This reservoir was so constructed as to allow saturation of the liquid contained in it with any desired gas, provision being made for bubbling in the gas at the bottom of the liquid. This second reservoir also made it possible to conduct a forced penetration run with two different penetrating liquids without interruption of the run or relief of pressure.

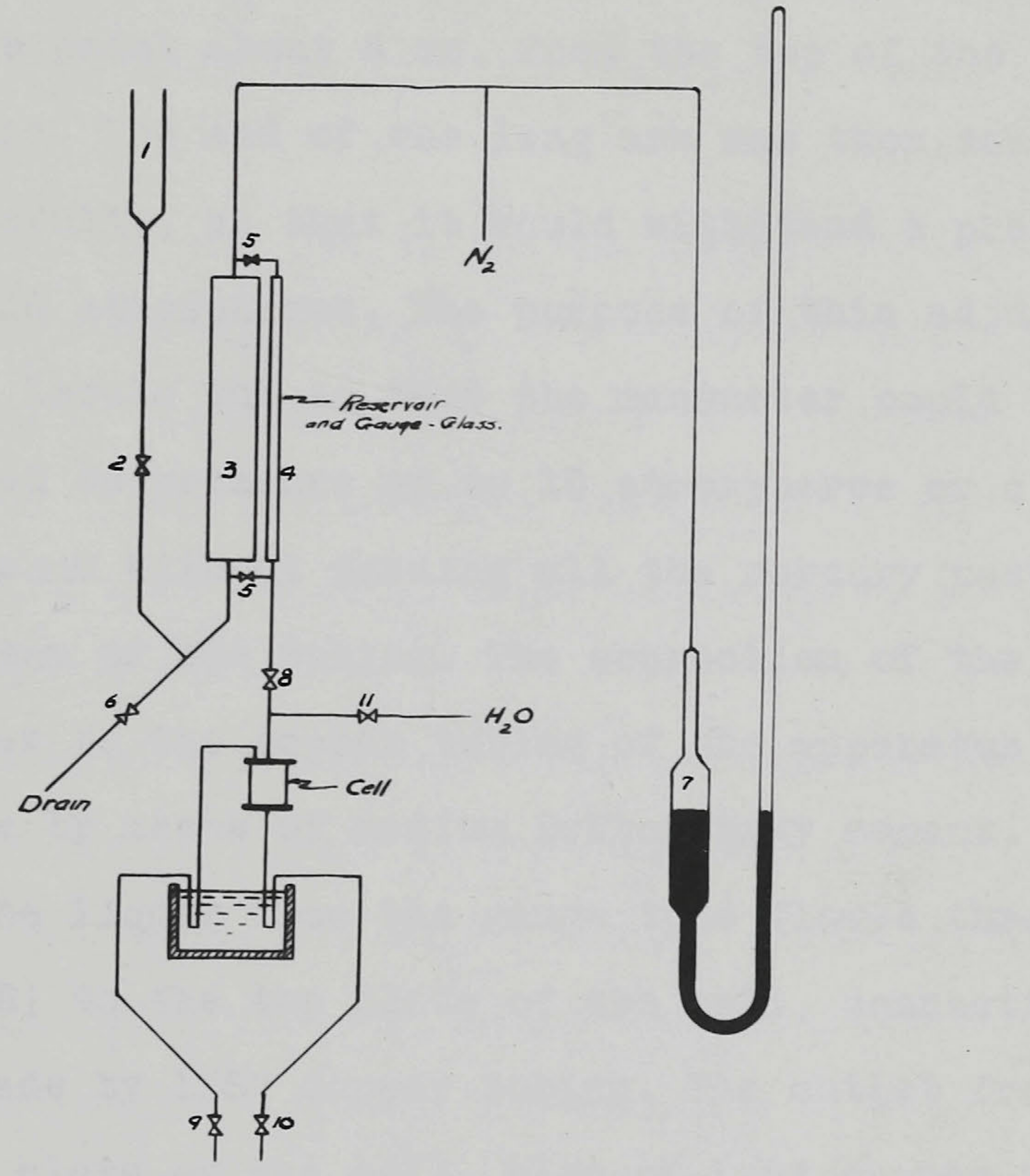
The small scale digester apparatus

For the small scale investigations of cooking conditions, the apparatus was much simplified, the set-up being shown diagrammatically in Figure 3. The small digester cell was the same as the penetration clamp except that the Allegheny metal ring was replaced by a 2" inside diameter Allegheny metal cylinder. Lead gaskets were used here too. The cooking liquor was introduced into the apparatus through a glass funnel (1), flowing by gravity through 1/2" brass pipe past a valve (2) into the cylindrical brass reservoir (3) and the gauge tube (4). The reservoir was of 2" brass pipe, 24" long, closed at both ends by brass caps. These caps were tapped to receive 1/2" close nipples which connected to 1/2" brass tees, the side arm of each tee acting as socket for a 1/2" brass water gauge valve (5). The upper tee was connected by a bushing to 1/4" brass tubing leading to the nitrogen cylinder. The lower tee led by a brass pipe to the glass funnel (1) as indicated, and also to an outlet valve (6). All the joints in this part of the apparatus were soldered.

The gauge glass was of heavy-walled 1/2" Pyrex tubing. It was fastened into the valves by winding several turns of electrician's tape about each end and surrounding this by graphite-asbestos packing. No trouble from leakage was experienced. By means of the water gauge valves (5), the liquid in the gauge tube could be separated from that in the reservoir. The tube was calibrated in terms of volume to length.

The pressure on the liquid was provided by a cylinder of nitrogen gas connected through a reducing valve to the apparatus. The pressure was registered on a mercury manometer (7). This was composed of two arms, connected at the bottom in a U. Both arms were of 9 mm. Pyrex tubing, but the short arm near the top had a cylindrical reservoir of Pyrex, 25 mm. in diameter and 20 cm. long. The total length of the

Figure 3.



COOKING SET-UP
SIMPLIFIED
PENETRATION
APPARATUS

short arm was slightly more than 76 cm. The long arm was about 250 cm. long and was of uniform diameter throughout its length. This glass had been thoroughly cleaned and dried, and redistilled mercury poured into it until the level in the arms was at a point about 6 cm. from the top of the reservoir. The end of the long arm was then sealed off carefully, so that it would withstand a pressure of 10 atmospheres. The purpose of this adjustment of levels was so that the manometer could be subjected to pressure up to 10 atmospheres or a high vacuum without forcing all the mercury past the bottom of the tubing. The connection of the manometer to the copper tubing of the apparatus was made by means of medium DeKhotinsky cement.

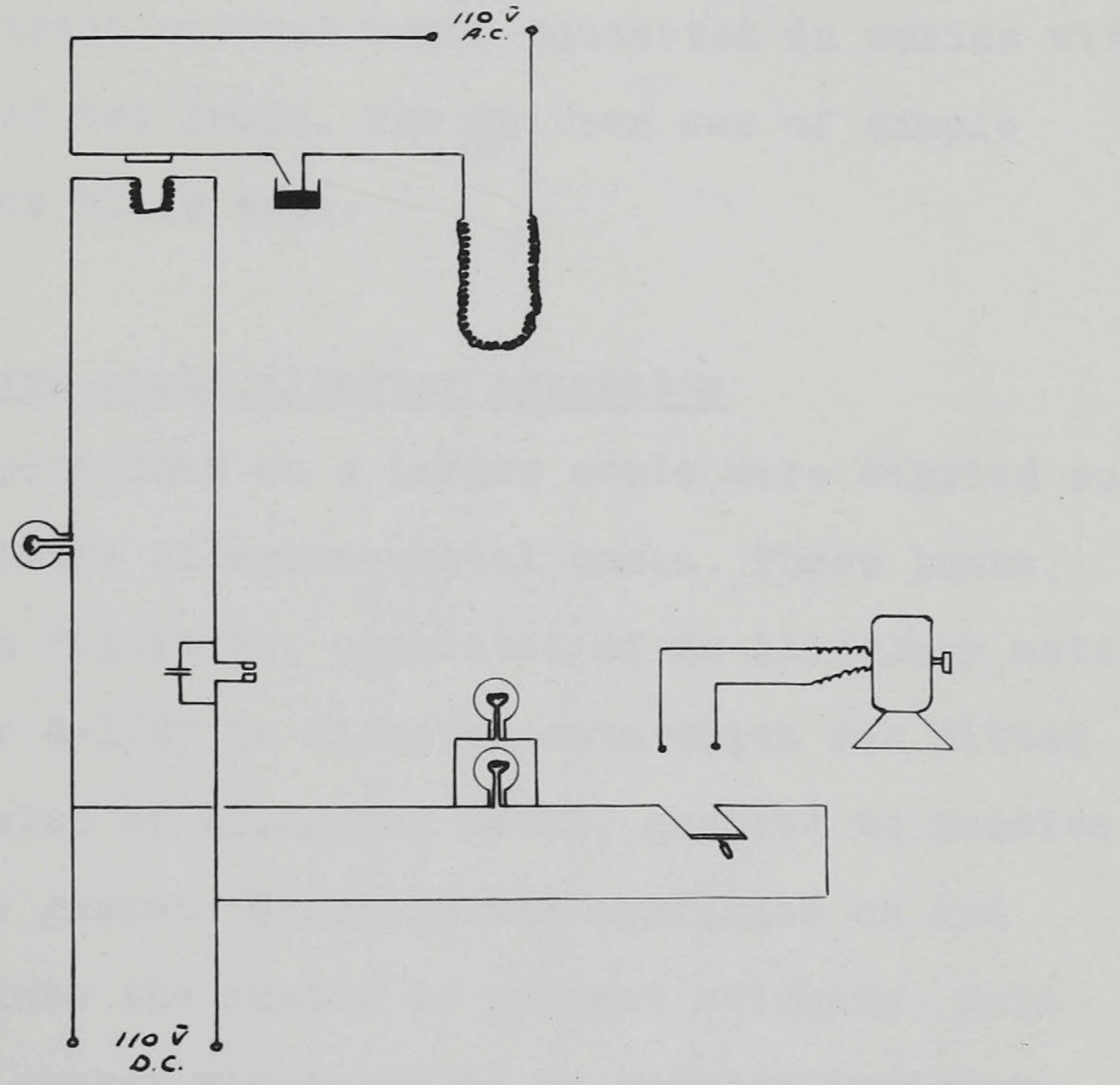
The liquor from the gauge tube flowed through valve (8) to the top plate of the cell, connection being made by 1/8" copper tubing. The outlet from the top plate of the cell, also of 1/8" copper tube led, through a cold water bath, to an outlet valve (9). Another outlet from the bottom plate led through the same water bath to outlet valve (10). Provision was at first made for a connection from the water main to the bottom of the cell. Due to leakage troubles from the bottom connecting block, this was later eliminated and replaced by a single outlet pipe connected by a compression coupling.

Minor changes were made from time to time in the cell connections to serve specific purposes. These changes will be described in the experimental section in connection with the particular runs involved.

The cell was heated and maintained at constant temperature during a run by a thermostatically controlled bath containing 14 quarts of glycoline. This liquid was quite satisfactory except for a strong tendency to give fumes at high temperatures after prolonged use.

The wiring arrangement for heating and stirring is shown in Figure 4. The bath was heated by means of 800 watt, 110 volt "Calrod" elements, bent to fit the bath. These elements were of resistance wire, insulated in silica and sheathed in metal. At first, two such elements were used in parallel, but it was later found more convenient to use a single element in conjunction with gas burners. Considerable trouble due to short-circuiting was overcome by surrounding the element with 2" lengths of Pyrex tubing. This eliminated all trouble from this source and did not introduce any excessive lag

Figure 4.



WIRING DIAGRAM
OF
PENETRATION APPARATUS

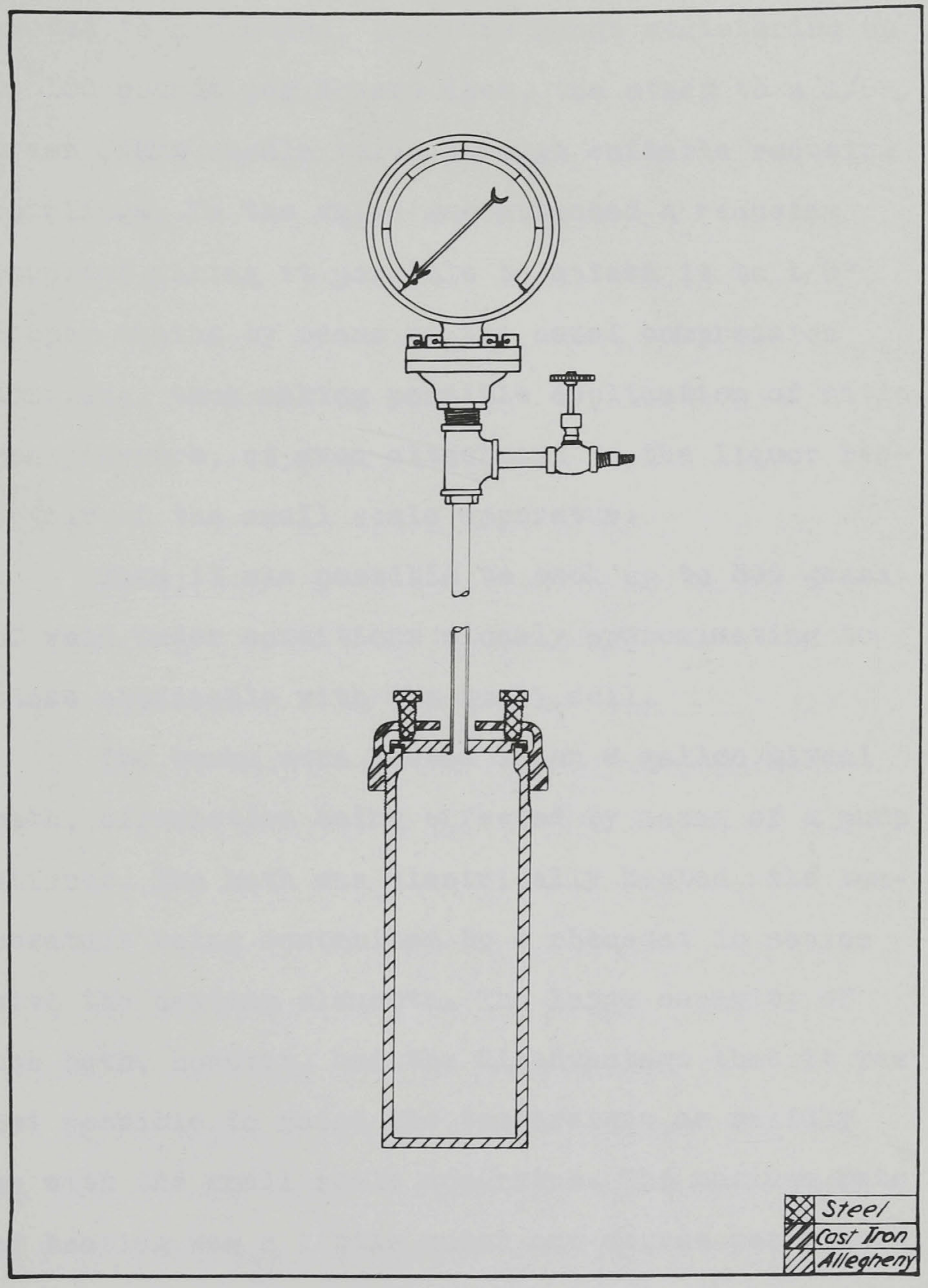
in temperature control. Regulation of the heating current was provided by a DeKhotinsky thermoregulator connected in parallel with an electrolytic condenser of aluminium plates in a solution of sodium bicarbonate, the regulator actuating a small relay to make and break the heating current.

Stirring was provided by a 1/8 H.P. shunt-wound direct current motor connected in series with a bank of two lamps. The stirrer was of simple propellor blade type.

The larger scale digester apparatus

Operations on a larger scale were carried out in two-litre Allegheny metal bombs. These bombs, shown in Figure 5., consisted of an Allegheny metal cylinder 4-1/2" in diameter onto which was fitted a cap, also of Allegheny metal, grooved to receive a rubber gasket. Graphite was sprinkled on and rubbed into the rubber to prevent sticking. This type of gasket was found to be very satisfactory, whereas it was found impossible to prevent leakage with the ordinary fibre gasket. A 4-1/2" pipe cap was screwed onto the outside of the body of the bomb and was threaded to receive six 1/2" bolts which were screwed down onto the bomb cap proper,

Figure 5.



thus making a tight seal. From the bomb cap, a 1/2" pipe led to a tee, one arm of which was connected to a chemical pressure gauge registering up to 150 pounds per square inch, the other to a 1/8" brass Crane needle valve through suitable reducing couplings. To the valve was attached a reducing coupling making it possible to attach it to 1/8" copper tubing by means of the usual compression coupling, thus making possible application of nitrogen pressure, or even attachment to the liquor reservoir of the small scale apparatus.

Thus it was possible to cook up to 300 grams of wood under conditions closely approximating to those obtainable with the small cell.

The bombs were heated in an 8 gallon glycol bath, circulation being effected by means of a pump stirrer. The bath was electrically heated, the temperature being controlled by a rheostat in series with the heating elements. The large capacity of the bath, however, had the disadvantage that it was not possible to raise the temperature as rapidly as with the small scale apparatus. The maximum rate of heating was a little under one degree per minute.

EXPERIMENTAL PROCEDURE

Forced Penetration Runs

The wood sample was cut into a disc about 1-5/8" in diameter and 7/8" thick and sandpapered to the exact thickness desired - 2 cm. The wood was then placed in a desiccator which was evacuated. After about half an hour's evacuation, water was allowed to rush in surrounding the wood which was held below the surface by a copper screen. The wood was allowed to soak overnight, usually sinking in the time allowed. This was done to avoid distortion of the wood by swelling in the clamp.

The soaked wood was cut by means of a circular knife to fit snugly in the ring of the clamp and forced into it until it was tight. The clamp was then firmly assembled.

A litre of the penetrating liquid was poured into the reservoir (2), FIG 1 or (15), and valve (16) closed. With valve (17) closed, and valves (7) and (9) open, a low pressure of nitrogen was applied to the system, until liquid came out of the outlet at valve (9), whereupon this valve was closed. By opening valve (18), the air at the back of the disc was flushed out at (10), after which valve (18) was again closed.

The clamp and connections on both sides of the wood were now full of liquid, and the apparatus ready for use in measuring the rate of penetration under differential pressure. Sutherland[5] found that there was a considerable interval before equilibrium rate of penetration was reached. The apparatus was left, therefore, under a low pressure differential for several hours, usually overnight, before making observations.

The actual run was started by adjusting the front pressure by means of the reducing valve on the nitrogen cylinder, the back pressure by means of the Alemite grease gun plunger, and the bath temperature by means of the thermoregulator. The lower water gauge valve (4) was then closed, cutting off the liquid in the gauge glass from that in the reservoir but allowing the nitrogen pressure to apply to both. Under the pressure differential, the liquid was forced through the wood, and by cracking valve (10) from time to time, the back pressure could be maintained at the desired value. At definite time intervals, usually of ten or fifteen minutes, the level of the liquid in the gauge tube was read, from which could be calculated the rate of penetration. Readings were taken until a constant rate of penetration was reached; then one or other of the variables was altered and readings resumed again until constant rate.

In the case of cooking experiments using forced penetration of the above type, the procedure differed from the above in that the rate of flow of liquor was kept constant at some predetermined value by adjusting the back pressure which had to be raised more or less continuously throughout the run as the wood became increasingly softened by cooking.

Small scale cooking runs

The weighed chips were placed in the cell, and the latter assembled tightly and carefully to avoid leakage. In practically all the runs reported, the cell was evacuated for 30 minutes by means of a water suction pump connected to the outlet valve (10) Fig 3. The pump was connected to the cell through a glass tee, the third arm of which led to a differential mercury manometer which gave a measure of the pressure and also, when the pump was shut off, revealed any leakage of the cell. At the end of the evacuation period, valve (10) was closed and valve (8) opened, allowing the liquor to fill the cell. In those runs where pre-evacuation was not carried out, the air in the cell was allowed to escape by opening valve (9) when filling the cell with liquor.

After the cell had been filled with liquor, the nitrogen pressure was raised to the desired level, and the cell carefully inspected for leaks. The oil bath was raised about the cell and the temperature raised at the desired rate to the desired maximum.

In some of the runs, replacements of waste liquor by fresh liquor were made during the course of the run. This was done by withdrawing samples from valve (10), the gauge tube, valve (5) being closed, showing the volume of liquor being withdrawn.

At the end of the run, the oil bath was lowered away from the cell, valve (8) closed, and the cell surrounded by a pail of cold water. At the end of about five minutes, valves (10) and (11) were opened and the cell flushed out with water. The cell was then dismantled, the chips were removed and treated as described below.

Larger scale cooking runs

The usual procedure when cooking in the two-litre bombs was to place the weighed chips in the bomb, place over them a perforated Allegheny metal plate (to prevent the chips from floating in the liquor) and then assemble the bomb. The bomb was then evacuated through the valve. At the end of the evacuation period, the valve was closed, a rubber tube attached to the valve outlet and filled with liquor, care being taken to expel all air bubbles from the tube. The end of the rubber tube was placed below the surface of a measured amount of liquor, the valve opened and the liquor allowed to be sucked into the bomb. The valve was then either left open and the bomb allowed to come to atmospheric pressure, or closed and connected to the nitrogen tank and the pressure built up to the desired value, after which the bomb was placed in the glycol bath and heated. During the cook, the pressure was maintained at the desired maximum by cracking the valve to allow the escape of gas. At the conclusion of the run, the bomb was quenched in cold water and opened. The chips, after separation from the liquor and washing on a Büchner funnel, were treated as described below.

Preparation of raw materials and treatment of products

(a) Small scale cooks

The forced penetration runs and a few of the preliminary cooks were made on jack pine and white spruce. All the rest of the investigation was carried out on black spruce, since a larger supply was available and a wider variety of specimens could be obtained. All the wood was supplied by the Forest Products Laboratories, mostly in the form of well seasoned, air dry 4" x 4" bolts. The bolts were cut by a band saw into transverse sections slightly more than 3/4" thick and sandpapered down to exact thickness. The chips were cut by hand to the desired shape.

Moisture determinations were made on each sample by drying in an oven at 105°C. for at least 12 hours. Density measurements were also made on the specimens. This was done by weighing and correcting the weight for moisture content, and measuring the volume either by direct measurements of the linear dimensions of an accurately cut block or, in the case of small samples, by immersion in mercury . The densities reported are given by the bone-dry weight divided by the air-dry volume.

The cooking liquor was prepared by suspending slightly more than the theoretical amount of lime required for the concentration desired in water and bubbling sulphur dioxide gas through the suspension for a short time after all the lime had dissolved. A good grade of lime (either Merck's or Schuchardt's) was used. The sulphur dioxide was washed by bubbling it through a solution of barium chloride in dilute hydrochloric acid and then through distilled water. Later, through fear of entrainment of hydrochloric acid into the cooking liquor, this washing train was replaced by a solution of barium hydroxide. The cooking liquors were analysed by the standard Winkler method[54], titration with iodine giving the "total" sulphur dioxide, and titration with sodium hydroxide and phenolphthalein giving the "free" sulphur dioxide. The "combined" sulphur dioxide was found by difference. The Sander method of titration with sodium hydroxide and methyl orange, with addition of an excess of mercuric chloride after the first end-point, was tried but could not be made to give satisfactory results.

The concentrations in the cooking liquor were adjusted by dilution to give the desired value for "combined" sulphur dioxide, and by addition of more sulphur dioxide or removal of it by evacuation to arrive at the desired concentration of "free" sulphur dioxide.

In a few instances, magnesia instead of lime was used as the base in the liquor. The procedure for preparing the liquor was exactly the same as with lime. Magnesium bisulphite liquors were used either to compare their action with that of calcium bisulphite liquors, or in cases where it was particularly desired to avoid all danger of precipitation which might occur with calcium bisulphite liquor.

The cooked chips were gently crushed between the fingers and put into about 800 cc. of distilled water. They were then disintegrated six minutes with a small Dumore disintegrator, consisting simply of a small metal propeller driven by a high speed motor. Only the definitely undercooked shieves resisted this treatment, the cooked fibres being completely separated. The pulp thus produced was filtered on paper in a Büchner funnel and washed twice by suspension in about 500 cc. of distilled water.

A judicious portion of the final suspension (chosen so as to contain 1.1 to 1.35 grams bone-dry fibre) was then made into a test sheet on the

British sheet machine according to standard procedure[8]. These sheets were then tested for bursting strength on a Mullen tester according to standard procedure[9]. The bursting strength ratios reported are calculated on the basis of a ream of 500 sheets 25" x 40" (standard weight 47.5 pounds).

The remainder of the pulp was filtered off and dried at least two hours in an oven at 105°C. Its weight added to the weight of the test sheet (corrected for moisture content) gave the total yield of pulp. The percentage yield was given by the bone-dry weight of pulp divided by the bone-dry weight of the chips cooked.

All the strength values and yields reported are based on the whole pulp including shieves. Since the quantities of pulp handled were of the order of three to four grams, no facilities were available for screening such small amounts. Consequently, no values for the percentage of screenings can be reported.

Lignin determinations were carried out on the dried pulps according to the method of Potter and Ross[10]. Since it was desired to conserve small samples of the pulps for possible future examination, single determinations were made in most cases. Doubtful cases were checked by duplicate determinations.

The yield of cellulose was calculated on the assumption that the pulp contained only cellulose and lignin, the yield of cellulose, therefore, being given by

$$\frac{\text{Yield of pulp x (100 - \% lignin in pulp)}}{100}$$

The residual lignin calculated on the basis of the original wood was given by Yield of pulp x % lignin in the pulp. These latter values are reported in the tabulated results under the column heading of "Residual Lignin".

Attempts were made to determine the tearing strength of the pulps, but, due to the small size of the samples, the values had to be rejected as unreliable. Tearing strength tests were made on some of the larger scale cooks, but did not seem to give any important information.

Microscopic examination of the fibres was occasionally resorted to; the observations, where noteworthy, have been included in the discussion of results.

(b) Larger scale cooks

The wood used for this scale of operation was not fashioned into chips by hand, but cut by a chipper as in industrial practice. This involved appreciable variation in the dimensions of the chips.

Preparation of the cooking liquor was effected by the same procedure as for the small scale cooks.

The cooked chips were reduced to pulp by treatment for five minutes in a Canadian disintegrator and the resulting pulp screened through a diaphragm screen with 0.009" slits. The screenings were dried in the oven at 105°C. and weighed. The screened pulp was suspended in 30 litres of water, and consistency tests made on this suspension to calculate the pulp yield. This screened pulp was sometimes subjected to further treatment, in which case mention has been made under the specific runs involved.

EXPERIMENTAL RESULTS AND DISCUSSION

The writer has felt it preferable to present discussion of results immediately following the group of runs involved rather than at the end of the thesis, thus avoiding much tedious cross-reference. A general discussion of all the results will be found at the end of the thesis.

As the amount of experimental data to be presented is rather large, detailed observations have been omitted and tabulation resorted to as far as was thought compatible with clarity.

The numbers of the individual runs give the order in which the experiments were performed. However, it was thought advisable to diverge from a strict chronological order in a few instances to achieve a more logical sequence in the development of the investigation.

Also many runs have been entirely omitted. These were of an exploratory nature and though yielding much useful information to the writer in arriving at final experiments, no useful purpose would be served by including them in this thesis.

FORCED PENETRATION

Among the results of Sutherland[5] mentioned in the introduction, those on the forced penetration of gases through wood are immediately noteworthy. It was found that whereas gases penetrated seasoned wood easily, wet wood strongly resisted gas penetration. In the course of sinkage studies, Saunderson[7] observed that removal of air contained in the wood specimens, by evacuation, very greatly reduced the time taken by these specimens to sink when immersed in liquid at atmospheric pressure. These two facts pointed to the conclusion that the discontinuity resulting from the simultaneous presence within the wood of two phases, one gaseous and one liquid, caused a very marked reduction in the rate of penetration. It appeared interesting to attempt to measure rates of penetration under conditions where such a discontinuity could be maintained, that is to say under conditions where a gas and a liquid could be forced through wood simultaneously and continuously; it appeared preferable to establish conditions such that the discontinuity in question might be made to originate spontaneously within the wood fibres themselves. The use of a saturated solution of a gas in water, such that, on release of pressure, the gas would come out of solution in appreciable amount suggested itself; carbon dioxide was the obvious choice for this purpose.

Under such conditions, one would expect that, providing the gas did come out of solution as the pressure gradient was traversed, the rate of penetration observed would be much less than that for water alone. If, however, supersaturation was encountered and the gas came out of solution only when the solution emerged from the wood - which was quite likely to occur at low pressure differentials - then one would expect the rate of forced penetration to be substantially the same as that for water until the pressure differential became high enough to overcome this supersaturation effect, whereupon a break in the rate of penetration - pressure differential curve would be expected. These predictions are based, of course, on the assumption that the gas solution would be saturated at the higher, or driving, pressure.

"Two-phase" forced penetration

By this term is meant the simultaneous forced penetration of both a gas and a liquid through wood. The rate of penetration - pressure differential curve was first determined for water alone, and then water and a saturated aqueous solution of carbon dioxide were forced through the chip alternately.

Run #1

Wood - Jack Pine heartwood, unseasoned, 3/4" chip.
Penetrating liquid - Water.
Temperature - Room.

Pressure differential atmospheres	Rate of penetration cc./minute
2	0.078
4	0.226
6	0.332

Run #2

Wood - same chip as for Run #1.
Penetrating liquid - alternately water and saturated solution of carbon dioxide.
Temperature - Room.

Pressure differential atmospheres	Rate of penetration cc./minute	
	Water	CO_2 soln.
2	0.082	0.063
4	0.179	0.164
5	0.250	0.218
6	0.308	0.221

After the last carbon dioxide solution penetration, the sides and lower third of the chip were considerably lighter in colour than the rest of the chip and had not its soaked appearance.

The results obtained were very gratifying in that the phenomena expected were manifested. The decrease in the rate of forced penetration on evolution of gas within the wood was quite marked. It is explainable by postulating the formation of a system known as a Jamin's tube[13]. This consists of a capillary tube filled alternately with drops of liquid and bubbles of gas. It has been observed that, in such a system, on application of pressure, the shape of the menisci is altered in such a way that less pressure is transmitted by the gas bubbles than is applied to them, so that the rate of flow is less than if the tube were completely filled with liquid. The importance of this phenomenon will be brought out in later experiments.

At pressure differentials below that corresponding to gas evolution, the rate of penetration of the carbon dioxide solution was slightly less than that of water. This is in agreement with the results of Sutherland[5] who found that the rate of penetration decreased with decreasing pH of the penetrating liquid.

Runs #3 and #4 were carried out to confirm the results discussed above.

Run #3 (Figure 6.)

Wood - Jack Pine heartwood, unseasoned, 3/4" chip.
Penetrating liquid - Water,
Temperature - Room.

Pressure differential atmospheres	Rate of penetration cc./minute
2	0.045
4	0.170
5	0.280
6	0.366

Run #4 (Figure 6.)

Wood - same chip as for Run #3.
Penetrating liquid - alternately water and saturated solution of carbon dioxide.
Temperature - Room.

Pressure differential atmospheres	Rate of penetration cc./minute Water	CO_2 soln.
2	0.045	0.033
4	0.174	0.153
5	0.251	0.226
6	0.318	0.245

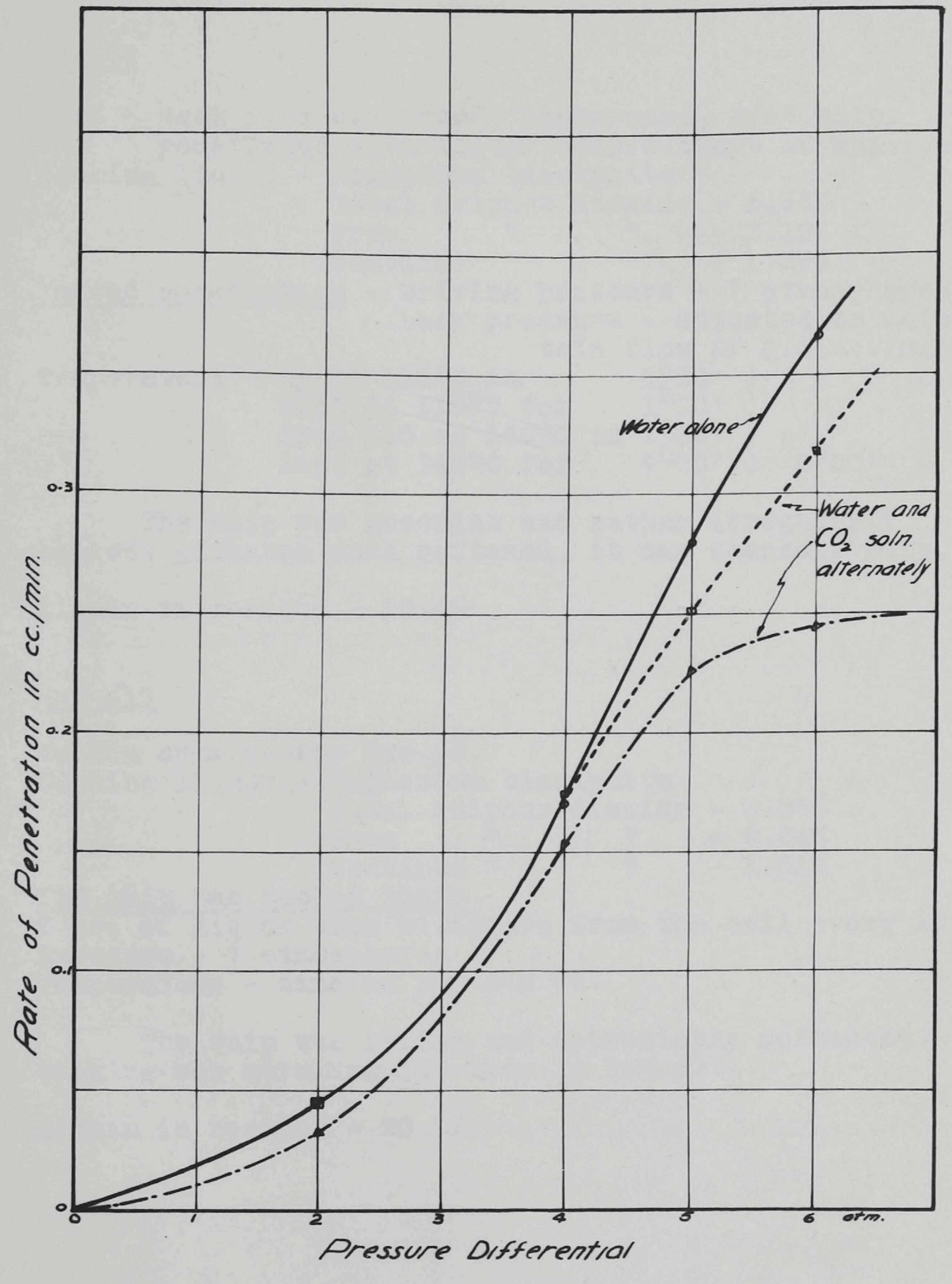
These two runs again illustrate the same phenomenon; the results are shown graphically in Figure 6.

COOKING EXPERIMENTS

Influence of continuous forced penetration

One of the specific objectives in mind, when the work was begun, was to determine, if possible, whether the time factor in cooking was influenced to a greater extent by penetration, both forced and natural, of the reagents than by the rate of the chemical changes involved. A few preliminary experiments were undertaken, therefore, to determine if a forced flow of cooking liquor through the wood during the cooking process would accelerate delignification, and thus justify the investigation of means

Figure 6.


Water alone
Water and
CO₂ soln.
alternately
Rate of Penetration in cc./min.
0
0.1
0.2
0.3
0
1
2
3
4
5
6
atm.
Pressure Differential

of arriving at better contacting of the wood and cooking reagents.

Run #9

Wood - Jack Pine heartwood, unseasoned, 3/4" chip, penetrated with liquor before start of run.
Cooking liquor - Magnesium bisulphite
Total sulphur dioxide - 3.66%
Free " " - 2.10%
Combined " " - 1.56%
Forced penetration - Driving pressure - 7 atmospheres
Back pressure - adjusted to maintain flow of 0.3 cc./min.
Temperature - up to 110°C in $1^h30'$)
kept at 110°C for $1^h00'$)
from 110 to 140°C in $1^h30'$)
kept at 140°C for $4^h00'$) $8^h00'$

The chip was greenish and rather irregularly cooked. Although much softened, it was scarcely pulp.

Lignin in residue - 10.4%

Run #10

Wood - same as for Run #9.
Cooking liquor - Magnesium bisulphite
Total sulphur dioxide - 3.55%
Free " " - 2.04%
Combined " " - 1.51%
The chip was cooked loose
3 cc. of liquor were withdrawn from the cell every 10'.
Pressure - 7 atmospheres
Temperature - same as for Run #9.

The chip was yellow and appreciably softened; cooking was more regular than in Run #9.

Lignin in residue - 20.8%

Run #16

Wood - White Spruce heartwood, air-dry, 3/4" chip
penetrated with liquor before start of run.
Cooking liquor - Magnesium bisulphite
Total sulphur dioxide - 3.65%
Free - 2.00
Combined - 1.65
Forced penetration - Driving pressure - 7 atmospheres
Back pressure - adjusted to maintain flow of 0.3 cc./min.
Temperature - up to 110°C. in $1^{h}30'$)
kept at 110°C. for $1^{h}00'$)
from 110 to 140°C. in $1^{h}00'$)
kept at 140°C. for $2^{h}30'$) $6^{h}00'$

The chip was much softened but irregularly cooked.

Lignin in residue - 11.6%

Run #12

Wood - same as for Run #16.
Cooking liquor - Magnesium bisulphite
Total sulphur dioxide - 3.52%
Free - 1.92
Combined - 1.60
The chip was cooked loose
3 cc. of liquor were withdrawn from the cell every 10'.
Pressure - 7 atmospheres
Temperature - same as for Run #16

Lignin in residue - 15.6%

Run #13

Wood - same as for Run #16.
Cooking liquor - Magnesium bisulphite
Total sulphur dioxide - 3.50%
Free - 1.75
Combined - 1.75
The chip was cooked loose
3 cc. of liquor were withdrawn from the cell every 10'.
The cell was evacuated 45' at 1.2 cm. of Hg. before introduction of liquor.
Pressure - 7 atmospheres
Temperature - same as for Run #16.

Lignin in residue - 15.5%

Run #15

Wood - same as for Run #16, but filled with water by forced penetration
Cooking liquor - Magnesium bisulphite
Total sulphur dioxide - 3.29%
Free - 1.61
Combined - 1.68
The chip was cooked loose
3 cc. of liquor were withdrawn from the cell every 10'.
Pressure - 7 atmospheres.
Temperature - same as for Run #16.

Lignin in residue - 25.5%

These results confirm Saunderson's[7] findings, with calcium bisulphite liquor, that forced penetration of cooking liquor through the wood itself results in more rapid delignification. This is to be expected since the concentration of the reagents is kept high and the products of reaction are removed by the flow of liquor through the wood.

Where the rate of heating is sufficiently slow to allow satisfactory penetration before the critical cooking temperature is passed, preliminary evacuation of the chip appears to have little effect.

When the chip is filled with water previous to cooking, entrance of the reagents into the wood is possible only by natural penetration - diffusion - and in this case, very little cooking takes place even at the end of six hours.

Influence of preliminary evacuation

In view of the results of the forced penetration experiments with carbon dioxide solutions, it was felt that preliminary evacuation of the chip should allow much more rapid penetration of the cooking liquor and hence more rapid rise to cooking temperature with possibly complete elimination of the "penetration period" at 110°C. The following runs were carried out to test this idea.

Run #18

Wood - White Spruce heartwood, 3/4" chip
    Density - 0.39
    Moisture - 7.0% (based on bone-dry weight)
Cooking liquor - Magnesium bisulphite
    Total sulphur dioxide - 4.85%
    Free - 3.50
    Combined - 1.35
The chip was cooked loose.
5 cc. of liquor were withdrawn from the cell every 10'.
Pressure - 7 atmospheres.
Temperature - up to 140°C. in 20'
    kept at 140°C. for $2^h30'$

No preliminary evacuation was used.

The chip was severely burned in the centre. It was soft and white on the outside but hard and brown in the centre.

in the centre

Lignin in residue - 31.8%

Run #19

Wood - same as for Run #18.
Cooking liquor - Magnesium bisulphite

Total sulphur dioxide	4.85%
Free	3.43
Combined	1.42

The chip was cooked loose.
5 cc. of liquor were withdrawn from the cell every 10'.
Pressure - 7 atmospheres
Temperature - same as for Run #18.
The cell was evacuated 30' at 1.2 cm. of Hg. before introduction of liquor.

The chip was very soft and very evenly cooked. There was not the slightest indication of burning.

Lignin in residue - 6.1%

Run #20

Same conditions as for Run #19 except
Cooking liquor - Calcium bisulphite

Total sulphur dioxide	4.70%
Free	3.30
Combined	1.40

Here again a very soft pulp was obtained without any indication of burning.

Lignin in residue - 7.9%

Run #21

Same as Run #20 but without preliminary evacuation
Cooking liquor - Calcium bisulphite

Total sulphur dioxide	4.65%
Free	3.20
Combined	1.45

The chip was burned severely in the centre.

Lignin in residue - 21.6%

Run #22

Same as Run #20 but without preliminary evacuation and with chip which had previously been filled with water by forced penetration.
Cooking liquor - Calcium bisulphite
Total sulphur dioxide - 4.92%
Free - 3.52
Combined - 1.40

The chip was very severely burned in the centre.

Lignin in residue - 33.5%

Runs #18-22 constitute a series. A second series is reported below with more complete data on the pulps produced.

Run #47

Wood - Black Spruce heartwood, 3/4" chip
Density - o.35 Moisture - 6.0%
Cooking liquor - Calcium bisulphite
Total sulphur dioxide - 4.78%
Free - 3.38
Combined - 1.40
The chip was cooked loose.
20 cc. of liquor were withdrawn from cell every 40'.
Pressure - 7 atmospheres.
Temperature - up to 140°C. in 30'
kept at 140°C. for $3^h30'$
The cell was evacuated 30' at 1.0 cm. of Hg. before introduction of liquor.

The chip was very soft and there was no burning.

Mullen Burst Ratio - 197%

Lignin in pulp - 5.0%

Yield of pulp - 49.5%

Yield of cellulose - 47.0%

Residual lignin - 2.5%

Run #44

Wood - same as for Run #47
Cooking liquor - Calcium bisulphite
Total sulphur dioxide - 4.78%
Free - 3.38
Combined - 1.40
The chip was cooked loose.
20 cc. of liquor were withdrawn from cell every 40'.
Pressure - 7 atmospheres.
Temperature - same as for Run #47.
<u>No preliminary evacuation</u> was used.

The chip was hard and severely burned.

Mullen Burst Ratio - 27%
Lignin in pulp - 24.6%
Yield of pulp - 61.4%
Yield of cellulose - 46.2%
Residual lignin - 15.2%

Run #45

Wood - same as Run #47.
Cooking liquor - Calcium bisulphite
Total sulphur dioxide - 4.92%
Free - 3.54
Combined - 1.38
The chip was cooked loose.
20 cc. of liquor were withdrawn from cell every 40'.
Pressure - 7 atmospheres.
Temperature - up to 110°C. in $1^h30'$)
kept at 110°C. for $1^h00'$)
from 110 to 140°C. in $1^h00'$)
kept at 140°C. for $3^h30'$) $\underline{7^h00'}$

The chip was quite soft but appreciably burned in centre.

Mullen Burst Ratio - 146%
Lignin in pulp - 8.7%
Yield of pulp - 49.0%
Yield of cellulose - 44.7%
Residual lignin - 4.3%

The work was next carried out on the larger scale of operations so as to afford comparison with the results obtained on the small scale.

Run #55

Made in two-litre bomb.

Wood - Black Spruce
Average chip length - 5/8"
Density - about 0.42, all chips from same log.
Moisture - 11.8%
Cooking liquor - Calcium bisulphite
Total sulphur dioxide - 5.20%
Free - 3.71
Combined - 1.49
Pressure - maintained at maximum of 95 lbs./sq.in. by relief.
Temperature - up to 140°C. in $1^h30'$
kept at 140°C. for $2^h15'$
The bomb was evacuated 30' at 1 cm. of Hg. before introduction of liquor.

The pulp was slightly raw and the screenings high. There were only a few burnt chips, practically all the screenings being undercooked chips.

Mullen Burst Ratio of
Pulp treated in mill - 101%
Pulp re-disintegrated in British disintegrator - 137%
Pulp re-disintegrated in lab. disintegrator - 139%

Lignin in pulp - 5.0%

The yield of pulp was not determined.

A few of the cooked chips were treated by the usual small scale procedure. Whereas the bulk of the pulp was markedly pink, the pulp thus made was very white.

Mullen Burst Ratio - 146.5%
Lignin in pulp - 6.6%

The discrepancy in the two lignin values is due to the removal of screenings which are, of course, high in lignin.

Run #A17

Made in two-litre bomb.

Wood - Black Spruce
Average chip length - 3/4"
Density - 0.49
Moisture - 7.7%
Cooking liquor - Calcium bisulphite
Total sulphur dioxide - 5.12%
Free - 3.76
Combined - 1.36
Pressure - allowed to rise to 98 pounds/sq.in. No relief was used.
Temperature - up to 110°C. in $1^h00'$
from 110 to 140°C. in 45'
kept at 140°C. for $4^h30'$
The bomb was evacuated 30' at 1 cm. of Hg. before introduction of liquor.

The chips were uniformly cooked and very soft. The pulp was light in colour and definitely overcooked. There was very slight burning at the end of the cook.

Mullen Burst Ratio of pulp treated in mill - 88.5%
M.B.R. after redisintegration for 4' in lab. - 102%

Yield of screened pulp - 45.9%
Yield of screenings - 0.7%
Total yield - 46.6%

The same wood cooked in the small Allegheny metal cell gave pulp with a Mullen Burst Ratio of 111%.

The preceding group of runs leave no doubt that a preliminary evacuation of the chip greatly hastens penetration and allows a rapid rise to cooking temperature without burning occurring.

Many investigators have realized the importance of satisfactory penetration for some time; but none seem to have pointed out the extraordinary influence which it appears to exert on the quality of the resulting pulp. The abnormally high values for bursting strength indicated in some of the above experiments will be discussed in greater detail later.

Dealing with the question of penetration and its influence on cooking results, apart from the above remarks, a survey of the literature shows that, as early as 1913, Schwalbe[14] recommended the relief of digesters at 70°C. rather than at 110°C. to let out air expelled from the wood by the penetration of the cooking liquor, and suggested that penetration would thus be aided. The same investigator[15] described a new pulping process which consisted in obtaining complete penetration at low temperatures by keeping the wood at 45-50°C. for ten hours, and then cooking for three hours at a high temperature, a satisfactory pulp being obtained.

Miller and Swanson[16] found that a complete preliminary penetration was essential to avoid burnt cooks and to give uniform pulp. They reported also that application of sulphur dioxide gas pressure above the cooking liquor hastened penetration.

Enge[22] also stated that poor penetration resulted in a burnt cook. He also claimed that pressure alone is of little use in hastening penetration unless the air is first removed from the wood.

Edwardes[23] subjected chips to a vacuum of 25 inches for 10-30 minutes, allowed liquid to cover them and applied pressure up to 80 lbs./sq.in. for 15 minutes. Difficulty was experienced in measuring the extent of impregnation, but in no case was penetration complete with water, although this was observed with kerosene. Edwardes also found that penetration proceeded to the same extent , although more slowly, if the preliminary evacuation was not used, and that the pressure applied was of much greater importance. He too pointed out the detrimental effect of poor penetration on cooking results.

Saunderson[7] found that a preliminary evacuation enormously reduced the time taken by chips to sink in sulphite liquor.

The following abstract of an article by Hansen and Hazelquist[24] is given as a typical example of the diametrically opposed expressions of opinion with which one is continually confronted on making a survey of the literature on sulphite cooking:

> "Penetration is not a deciding factor in the handling of sulphite digesters, as it is nearly impossible to bring a commercial digester of any size to 110°C. before penetration of the chips is complete, unless the initial acid temperature is under 35°C. It is not necessarily

> true that complete penetration has not taken place because a large amount of "brown" chips are present at the end of the cook. These may have been caused by not having enough combined sulphur dioxide present, by local overheating, etc. If local overheating has been great enough, it is possible that chips be "browned" even though penetration has been thorough. In general, increase in acid temperature increases the rate of penetration, increase in free sulphur dioxide increases the rate of penetration of free sulphur dioxide to an even greater extent and somewhat increases the penetration of combined sulphur dioxide. Pressure above that necessary to hold the gas in solution has very little effect on penetration. Penetration is a straight line function of the time. A moisture content of 30-40% is most favourable for a quick and thorough penetration."

There is one obvious reason for such controversies; that is the frequent failure to distinguish between the two very different types of burning. Except in the most severe cases, a mere physical examination of the burnt chips will differentiate between the two types.

The first type of burning takes place at the beginning of the cook, in which case the outside of the chips will be light coloured, well cooked and easily defibered, whereas the centre will be dark and hard. It is now generally recognized that this type of burning is caused by faulty penetration, as will be discussed at greater length later.

The second type of burning is that which occurs at the end of the cook, and which is caused, as is well known, by exhaustion of the available lime in the liquor. Here,the chips present a uniform appearance and may be quite soft and easily defiberable, but their colour may range from a light to quite a dark brown depending on the duration of the cook after the disappearance of the available lime.

It therefore appeared interesting to further study this controversial point with a view to gaining some insight into the mechanism involved.

It has long been the fashion to attribute many of the troubles encountered in sulphite cooking to sulphuric acid formation in the cooking liquor, and many a mechanism has been proposed to account for the possibility of its formation. However, on searching through the literature, one is surprised to find the almost total absence of any direct experimental evidence to confirm this tradition.

Miller and Swanson[17] report a series of cooks in which the percentage of sulphur dioxide present as sulphur trioxide in the raw acid ranged from 0.03% to 0.12%. The maximum concentration reached in any cook was 0.28%, and this at the end of 15-3/4" hours. The pulps obtained were not burnt and of normal strength.

Miller[25] reports having obtained good pulps in high yield from cooks in which he added sulphuric acid and sulphates to the cooking liquor.

The question of liquor acidity is also interesting from another angle, that of the mechanism of the process. The principal reaction is generally accepted to be hydrolytic in character.

Miller and Swanson[18] studied the effect of hydrogen ion concentration of the cooking liquor by carrying out cooks with sodium bisulphite and various acids. They found that the removal of carbohydrate material increases with increasing hydrogen ion concentration. Lignin removal, however, they claimed varies with the amount of <u>ionized sulphurous acid</u>, which in turn they alleged is governed by any other acid which may be present in the liquor.

Hägglund[26] also stresses the importance of hydrogen ion concentration in lignin removal.

These and many other investigators seem to neglect the extremely important phenomenon that, as has been shown by Campbell and Maass[27], sulphurous acid is virtually completely <u>unionized</u> at the temperature of the sulphite cooking process. Consequently, hydrogen ions in the cooking liquor must have their origin in the strong lignin sulphonic acids formed or in sulphuric acid present in the liquor. In this connection, it might be pointed out that pH determinations carried out on the cold cooking liquor can be of little value in picturing what happens at cooking temperatures.

Influence of liquor acidity

The experiments reported below were carried out more particularly to observe the effect of liquor acidity on pulp strength.

These and all subsequent cooks were made with calcium bisulphite liquor.

Runs #243 - 248

Wood - Black Spruce heartwood, 3/4" chips
Density - 0.34 Moisture - 9.0%
Cooking liquor - Total sulphur dioxide - 5.15%
Free - 3.90
Combined - 1.25
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Added Reagent	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
247	0.05N H_2SO_4	123.5	6.4	47.1	44.1	3.0
248	0.05N Na_2SO_4	141	7.3	52.3	48.5	3.8
243	0.10N HCl	143	4.6	50.8	48.5	2.3
244	0.10N CCl_3COOH	133	6.9	53.0	49.4	3.6
245	0.10N $pCH_3-C_6H_4SO_3H$	158	4.7	49.3	47.0	2.3
246	None	154.5	4.0	50.2	48.2	2.0

Runs #253 - 255

Wood - Black Spruce heartwood, 3/4" chips
Density - 0.42 Moisture - 6.4%
Cooking liquor - Total sulphur dioxide - 5.24%
Free - 3.94
Combined - 1.30
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	H_2SO_4 in Cooking Liquor	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
255	Nil	160	2.4	45.5,	44.4	1.1
253	Trace	157	3.5	47.2	45.5	1.65
254	0.05 N	157	3.3	45.8	44.3	1.5

The liquor for Run #253 was fresh liquor prepared in the usual fashion.
The liquor for Run #255 was prepared from boiled distilled water and under an atmosphere of nitrogen.

These results are not particularly illuminating. With the wood of low density (0.34) sulphuric acid appears to cause a marked decrease in pulp strength, the other acids giving intermediate values. On the contrary, with the wood of density 0.42, the addition of sulphuric acid to the cooking liquor gave nearly unchanged strength. In a third series of runs of the same type, a marked increase in strength resulted on addition of both sulphuric acid and sodium sulphate. As these results, however, could not be reproduced, they are not reported here.

All the runs showed consistently decreased delignification on increase of cooking liquor acidity; the yield of cellulose was only very slightly altered, except in the case of Run #247.

The observations seem to indicate that the abnormally high pulp strengths, obtained by the abbreviated cooking procedure made possible by pre-evacuation, are not to be attributed to the elimination of sulphuric acid formation by removal of the oxygen of the air in the chips. The amount of sulphuric acid which could be formed thus is, in reality, very small when compared with that which is necessarily present in the usual cooking liquor due to oxidation by the oxygen dissolved in the water from which the liquor is prepared, to which must be added that which is inevitably formed by autoxidation. The hydrogen ion concentration arising from this source cannot be important in comparison to that due to the products of the reaction, the strong lignin sulphonic acids.

<u>Run #A1</u>

Made in two-litre bomb.

Wood - Black Spruce, low density.
Average chip length - 7/8"
Moisture - 10.5%

Cooking liquor - Total sulphur dioxide - 5.15%
Free - 3.78
Combined - 1.37

The bomb was evacuated 30' at 1 cm. of Hg.

Run #A1 (continued)

Pressure - Nitrogen pressure of 75 lbs./sq.in. applied
Then allowed to rise to max. of 110 lbs./sq.in.
Temperature - up to 140°C. in $1^{h}45'$
kept at 140°C for $2^{h}15'$

Mullen Burst Ratio of pulp treated in mill - 91%
M.B.R. after re-disintegration in lab. -119%

Yield of screened pulp - 41.9%
Yield of screenings - 1.2%
Total yield - 43.1%

Lignin in pulp - 4.9%

Run #A2

Same as Run #A1, except that the cooking liquor was made 0.1 normal with respect to sulphuric acid.

Mullen Burst Ratio of pulp treated in mill - 95.6%
M.B.R. after re-disintegration in lab. - 115.5%

Yield of screened pulp - 40.8%
Yield of screenings - 1.8%
Total yield - 42.6%

Lignin in pulp - 4.3%

The addition of sulphuric acid to the cooking liquor appears to have produced practically no change in cooking results on this scale of operation.

Experiments on relative reaction velocities

Numerous mechanisms for the organic reactions taking place in the course of the sulphite process have been suggested, and it is gratifying to note that many of the workers in this field are gradually reaching better agreement. A mechanism for the process, which is a cross-section of many researches has been outlined by Michel-Jaffard[28]. The majority of organic chemists seem to be agreed that the lignin of the wood first forms with the free sulphur dioxide of the cooking liquor a solid compound. This solid compound later passes into solution by some process which is mainly hydrolytic, and in which the base in the liquor plays a part. But nowhere in the literature can definite data be found on the relative rates of these reactions, data which would be important in arriving at a satisfactory explanation of the burnt cook (burning at the beginning of the cook).

Consequently, the following experiments were devised with a view to obtaining some idea of the order of magnitude of these reaction velocities.

The wood samples used for this purpose were transverse sections of 2 mm. thickness. Since the fibre length of spruce is of the order of 3 mm. this ensured that all the tracheids would have at least one end open, so that resistance to penetration caused by the bordered pit membranes would be eliminated. With such specimens, penetration would be practically instantaneous.

Run #225

Wood - White Spruce heartwood
Chip length - 2 mm.
Density - 0.41
Moisture - 12.0%
Cooking liquor - Total sulphur dioxide - 5.17%
Free - 3.87
Combined - 1.30
Pressure - 10 atmospheres.
Temperature - the oil bath was preheated to 140°C. and raised about the cell a few seconds before the cooking liquor was allowed to fill the cell. Then kept at 140°C. for $1^{h}30'$
The cell was evacuated 15' at 1 cm. of Hg.

The chips were still decidedly raw, but there was not the slightest indication of burning.

Run #226

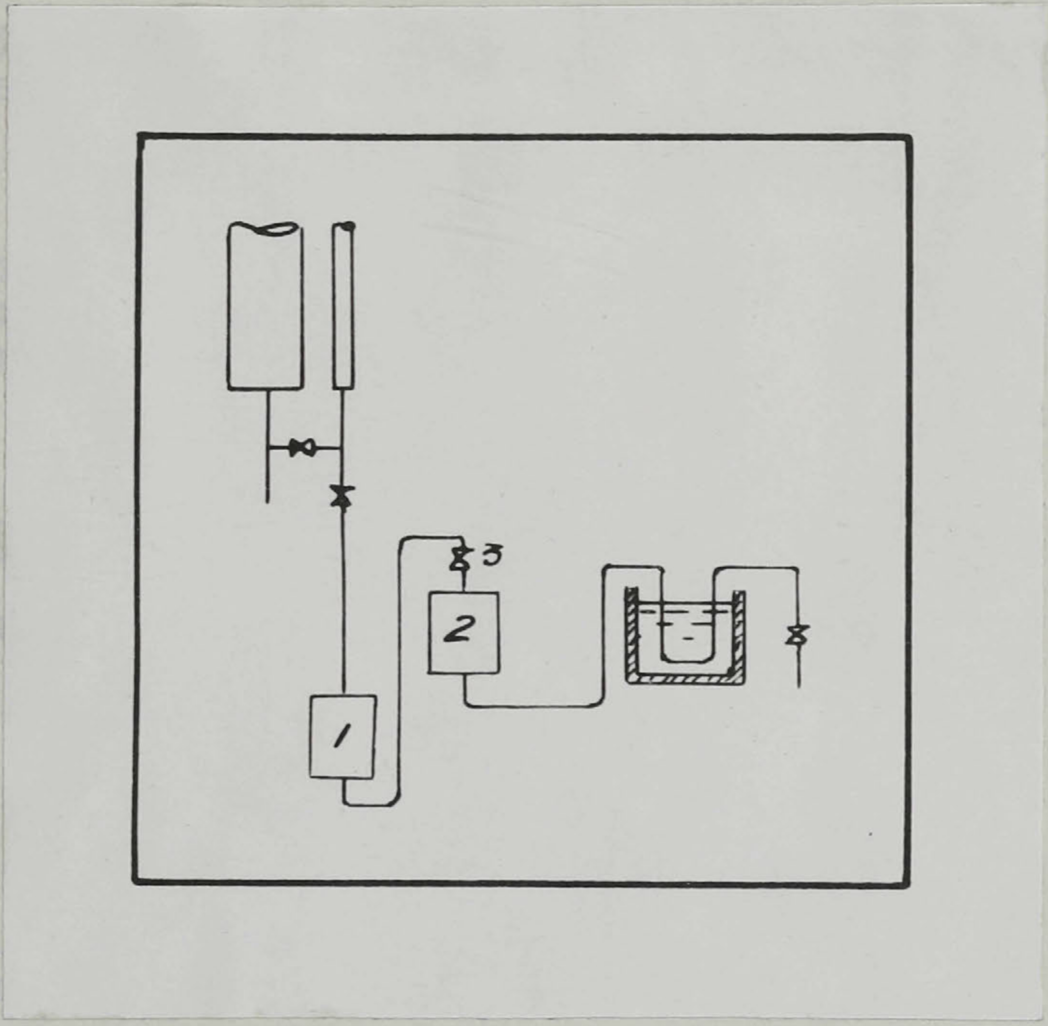
This run was a repetition of Run #225 except that the temperature was kept at 140°C. for $2^{h}00'$

Mullen Burst Ratio - 50.5%
Lignin in pulp - 13.7%
Yield of pulp - 61.9%
Yield of Cellulose - 53.4%
Residual lignin - 8.5%

The chips were considerably softer, and there was again no indication of burning.

These experiments, though very satisfactory, were not quite conclusive since penetration had actually taken place in the cold. Therefore, the apparatus was modified as shown below. Two cooking cells were connected in series and separated by a

1/8" brass needle valve(3). Cell (2) contained the wood chips. Cell (1) was placed at a lower level than cell (2) so that it could be immersed alone in the oil bath. The procedure was as follows. Both cells were evacuated to 1 cm. of mercury for 15 minutes. Then valve (3) was closed and cooking liquor was allowed to fill cell (1) which was then



immersed in the oil bath which had been preheated to 140°C. At the end of 15 minutes, the oil bath was raised to cover cell (2) and valve (3) opened, the cooking liquor filling cell (2). The liquor in cell (1) was replaced by the small amount of cold liquor remaining in the gauge tube and compressed nitrogen gas.

Run #227

Wood - White Spruce heartwood
Chip length - 2 mm.
Density - 0.41
Moisture - 12.0%

Cooking liquor -	Total sulphur dioxide	- 5.24%
	Free	- 3.88
	Combined	- 1.36

Pressure - 10 atmospheres.
Temperature - liquor preheated to 140°C. before introduction into cell.
kept at 140°C. for $2^h30'$

The chips were very soft, and there was not the slightest indication of burning.

Mullen Burst Ratio - 112.5%
Lignin in pulp - 4.7%
Yield of pulp - 52.5%
Yield of Cellulose - 50.0%
Residual lignin - 2.5%

Run #228

Repetition of Run #227 except

Wood - Black Spruce heartwood
Chip length - 2 mm.
Density - 0.54
Moisture - 8.4%

The chips were quite soft and there was again no sign of burning.

Mullen Burst Ratio - 92%
Lignin in pulp - 9.9%
Yield of pulp - 50.8%
Yield of cellulose - 45.8%
Residual lignin - 5.0%

The pulps from Runs #227 and 228 have lower strength than is usually obtained from short cooks with pre-evacuation. This is due to the mechanical cutting of the fibres in the course of the preparation of the samples. Brown[29] has shown that manufactured short fibres, i.e. short fibres made mechanically from long ones in contrast to naturally occurring short fibres, have lower strength than the original long fibres.

The last four runs, and especially Runs #227 and 228 show conclusively that the elimination of burning at the beginning of the sulphite cook is entirely a problem in penetration. In these runs, conditions were ideal for practically instantaneous complete penetration. Under these conditions, the cooking liquor may be preheated to 140°C. - i.e. 30 degrees C. above the "critical" temperature of 110°C before coming into contact with the wood, and still no burning occurs. Burning must therefore be attributed to incomplete penetration before the temperature has passed 110°C.

This does not imply that there cannot be an intermediate reaction, or several intermediate reactions, in the sulphonation of lignin preceding the final step of removal of lignin into solution; but it does establish that any such reaction, or reactions, must be rapid, or, at least, more rapid than that reaction which results in burning. Hence, in a commercial digester, the temperature must be raised slowly not because of the time taken by any so-called "protection" reaction to come to completion, but to allow complete penetration to take place, i.e. to allow the reagents to come together to make reaction possible.

Saunderson[7] has shown that penetration of the free sulphur dioxide is more rapid than that of the base, and it is known that free sulphur dioxide in the absence of base above 110°C will cause lignin to polymerize to a dark-coloured insoluble substance[55]. This, coupled with the experiments reported above, is sufficient to explain the burnt cook as being caused by the presence in the wood of free sulphur dioxide in absence of base above 110°C, this condition being brought about by incomplete penetration.

This explanation appears rational since it attributes the same cause to burning at the beginning of the cook as to burning at the end of the cook, the mechanism alone differing in each case. Burning at the end of the cook has been shown[19] to be due to the exhaustion of the combined sulphur dioxide, i.e. of the base, through reaction; and here again we have present in the wood sulphur dioxide in the absence of base at a temperature above 110°C.

[illegible]

Hrubesky and Chidester[30] have recently confirmed, by direct observations, Saunderson's[7] findings regarding the slower penetration of lime than of free sulphur dioxide, and also regarding the effect of temperature and acid concentration on rate of penetration. They found, moreover, that "a rather definite length of time, varying with conditions, is required to burn unpenetrated chips, when the critical temperature is exceeded. Chips very nearly penetrated may be completely penetrated before being burned when the rate of temperature rise is decreased after reaching the critical temperature." Hence, "some latitude in rate of temperature rise is permissible in passing through the critical temperature range on a cooking schedule." This confirms the conclusions drawn above, that the reaction, resinification or the like, which results in a burnt cook is slower than any intermediate reaction which may occur. These investigators also found that the critical temperature above which burning takes place varies somewhat, within fairly narrow limits, with cooking conditions.

Burning at the beginning of the cook is accompanied by a greater or less increase in the lignin content of the pulp, and by a reduction of cellulose yield depending on the severity of the burning. Free lignin sulphonic acid is soluble in water but, in acid medium, resinifies at temperatures above 110°C. to a dark insoluble compound which is no longer dissolved by sulphite liquor and which is reprecipitated on the fibres. Therefore, the mechanism of the burnt cook may be pictured as the formation of free lignin sulphonic acid (lime not having penetrated) which temporarily passes into solution and then precipitates out on the fibres, explaining the higher final lignin content and poor colour of the pulp. Since this reprecipitation takes an appreciable time, there will be always free acid in solution, so that the cellulose will be surrounded by a medium of higher acidity than is normal in the early stage of the cook. Hence, more cellulose hydrolysis will take place than in a normal cook and the final yield of cellulose will be lower than normal. Much the same phenomenon occurs in burning at the end of the cook on the disappearance of the available base and rise in acidity of the liquor.

Influence of Evacuation Pressure

Although other investigators have attempted to further penetration by pre-evacuation[23], no one has quantitatively measured the relation between the pressure of inert gas left in the wood and its influence on the progress of the cooking process. From the penetration mechanism pictured, it seemed likely that a critical pressure existed, above which the influence of the inert gas would prove to be a decided hindrance to penetration. Obviously, it is not possible to remove every trace of inert gas from a material such as wood which has adsorbing powers for even nitrogen and hydrogen gas[31]. It appeared probable that mere traces of inert gases would not exert any marked influence but that the effect would become extremely striking once the pressure reached a point where the size of the residual gas bubbles attained a size comparable with that of the passages through the wood.

The arrangement of apparatus used to regulate the evacuation pressure centered about a glass cross. One arm led to the outlet valve (10) of the cell and another to a water suction pump. The third arm was connected to a differential mercury manometer. The fourth arm led to a 3-litre glass bottle through the stopper of which was also fitted a simple bleed-in valve consisting of a piece of rubber tubing and a screw-cock.

Runs #56 - 61 (Figure 7.)

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.36
Moisture - 6.4%
Cooking liquor - Total sulphur dioxide - 5.00%
Free - 3.65
Combined - 1.35
Pressure - 7 atmospheres.
Temperature - up to 140°C. in 1^{h}00'
kept at 140°C. for 3^{h}00'
The cell was evacuated for 30'

Run No.	Evacuation Pressure cm. of Hg.	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
56	1	187	4.0	50.6	48.6	2.0
57	6	179.5	4.6	51.1	48.7	2.4
61	9	146	10.2	52.7	47.4	5.3
59	12	130.5	10.8	53.3	47.5	5.8
58	No evac.	---	----	59.6	----	---

Runs #62 - 66 (Figure 8.)

Same as Runs #56 - 61 except

Wood - Black Spruce heartwood
Chip length - 3/8"
Density - 0.52
Moisture - 7.0%

Run No.	Evacuation Pressure cm. of Hg.	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
62	1	123	6.6	55.0	51.4	3.6
63	6	134.5	6.8	53.0	49.4	3.6
64	12	120.5	7.0	53.9	50.1	3.8
66	24	113	8.3	54.3	49.9	4.4
65	No evac.	23.5	17.9	56.9	46.7	10.2

Figure 7.

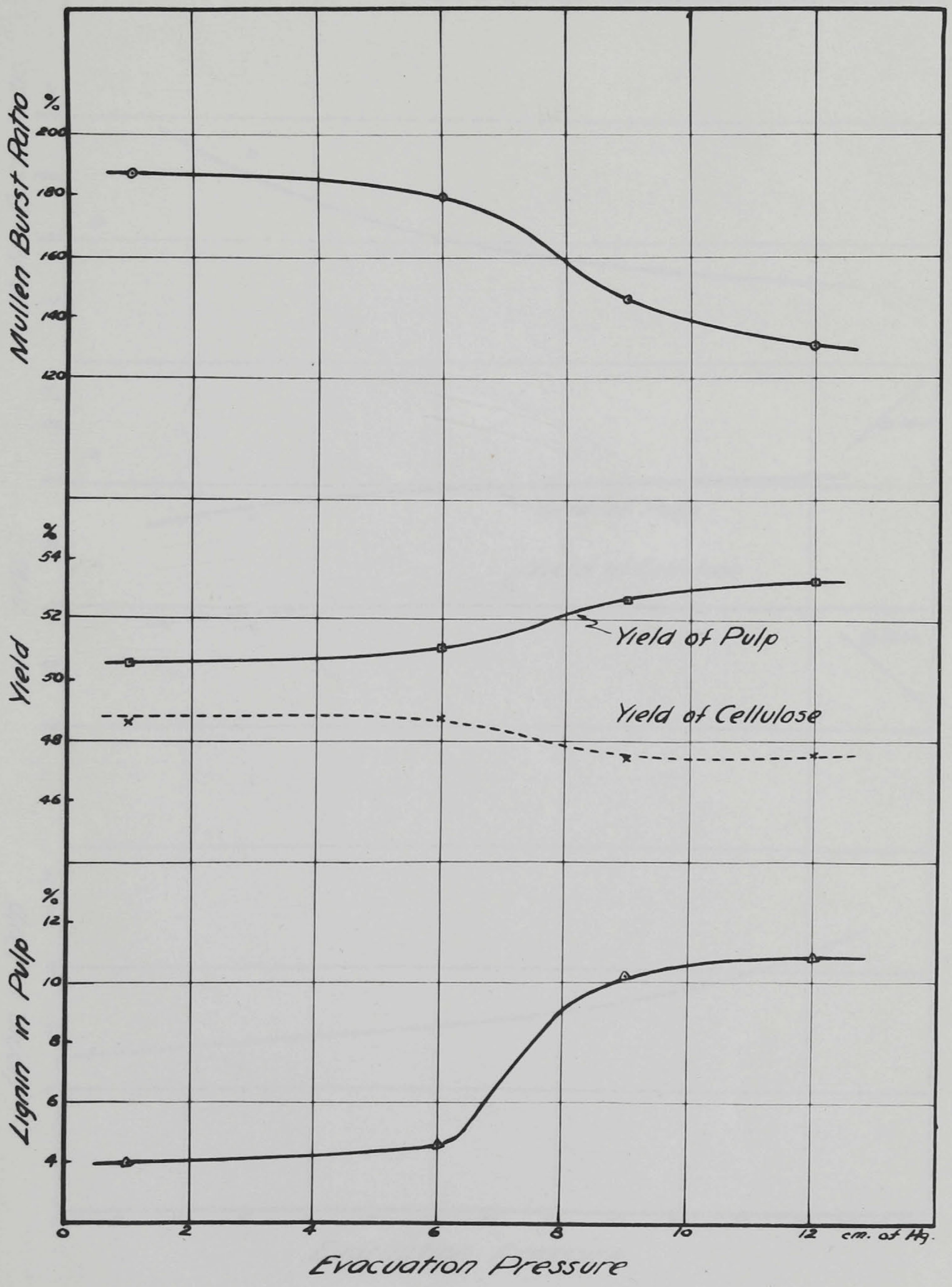
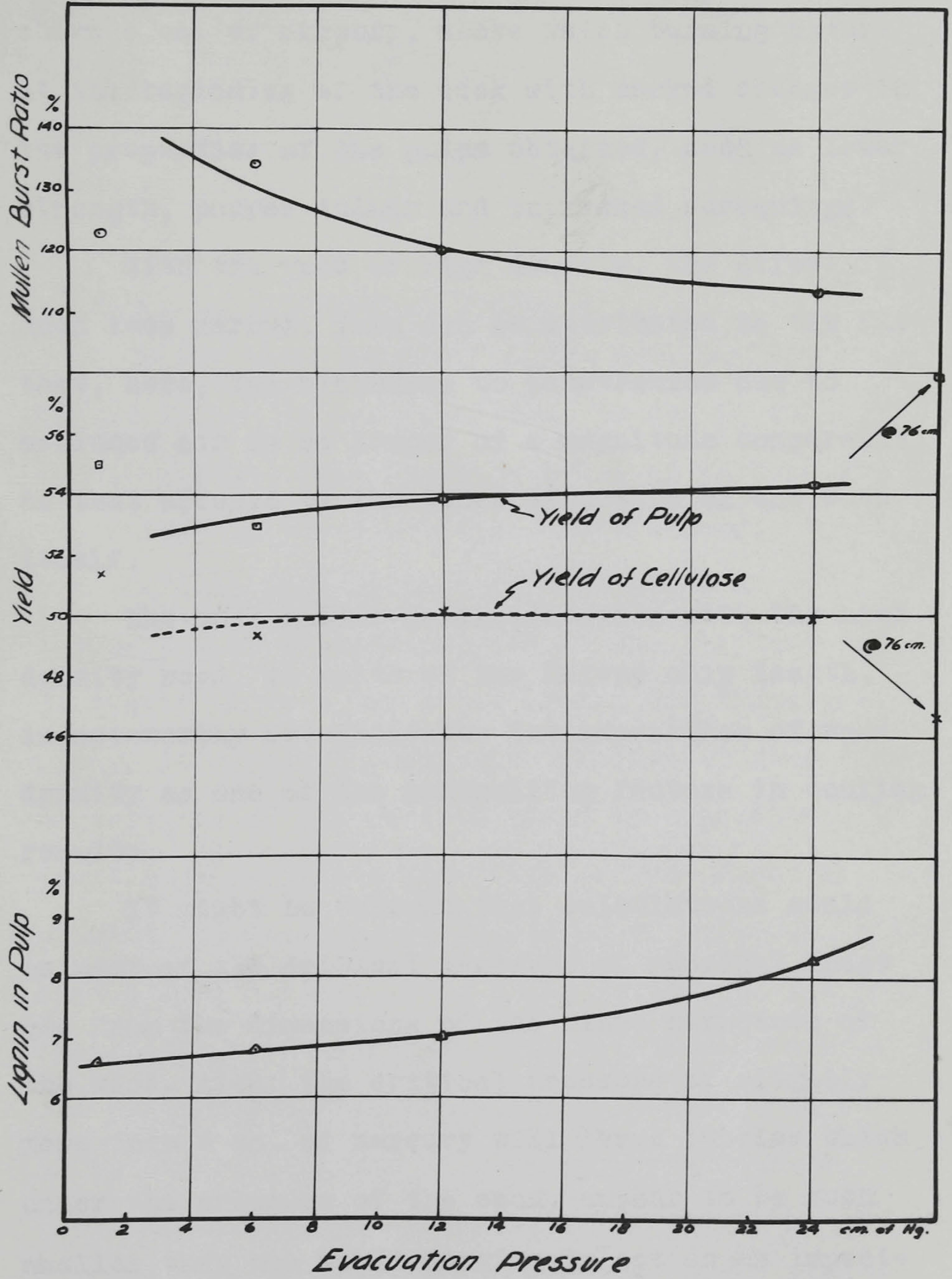

Mullen Burst Ratio
%
200
180
160
140
120
Yield
%
54
52
50
48
46
Yield of Pulp
Yield of Cellulose
Lignin in Pulp
%
12
10
8
6
4
0
2
4
6
8
10
12
cm. of Hg.
Evacuation Pressure

Figure 8.


Mullen Burst Ratio
%
140
130
120
110
Yield
%
56
54
52
50
48
46
Yield of Pulp
Yield of Cellulose
@ 76 cm.
@ 76 cm.
Lignin in Pulp
%
9
8
7
6
0
2
4
6
8
10
12
14
16
18
20
22
24
cm. of Hg.
Evacuation Pressure

With the wood of low density, there is a very definite critical evacuation pressure, slightly above 6 cm. of mercury, above which burning occurs at the beginning of the cook with marked changes in the properties of the pulps obtained, such as lower strength, poorer colour and increased screenings.

With the wood of high density, the effect is much less marked. This can be attributed to the fact that, here, the hindrance to penetration due to occluded air is no longer of a magnitude comparable to that offered by the dense structure of the wood itself.

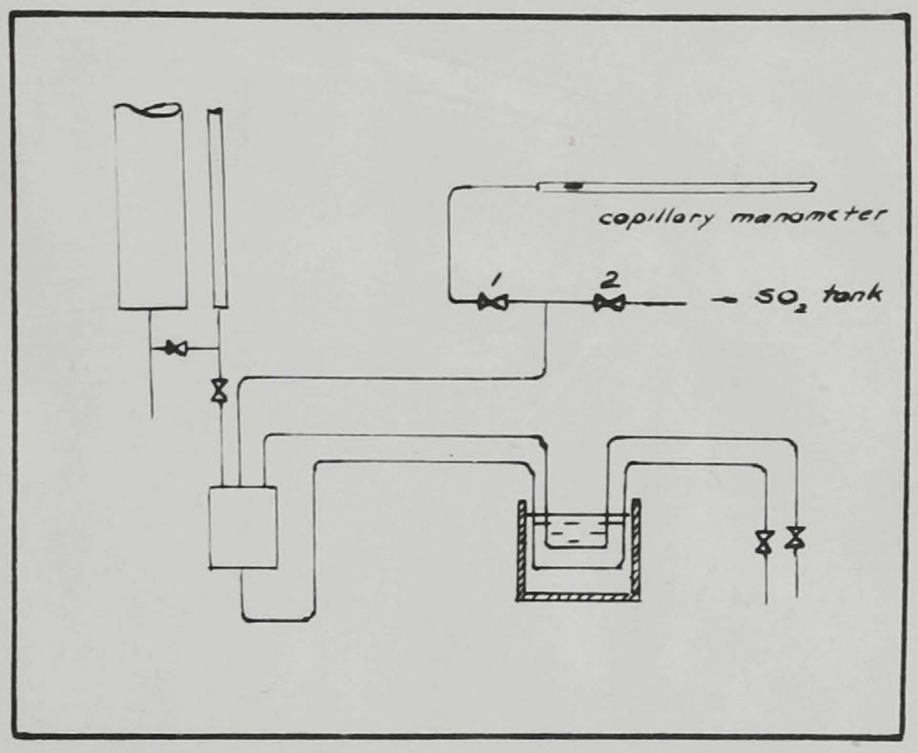
The much slower delignification with the high density wood, in spite of the halved chip length, is noteworthy and indicates the importance of wood density as one of the controlling factors in cooking results.

It might be thought that calculations could be made of the critical pressure of residual inert gas from the dimensions of the fibre structure of the wood. Also, the critical pressure of slightly more than 6 cm. of mercury will leave bubbles which, under the pressure of the cook, appear to be much smaller than one would imagine to act as an impediment to penetration. It must be remembered, however, that an inert gas serves as a nucleus into which the sulphur dioxide and water vapour from the cooking liquor will evaporate, and, as a result, the increased pressure in any cook is not effective in reducing the volume of the gaseous phase to that given by the inert gas volume.

Alternate pre-treatment procedure

Since pre-evacuation influences cooking procedure in the manner suggested, it was of interest to see whether this might be achieved in some way other than by pre-evacuation. Furthermore, since it was realized that present day digesters do not lend themselves to evacuation, due to the infiltration of liquor between the brick lining and the digester shell, it appeared desirable to discover other means of arriving at the results given by evacuation. It was thought that the same final effect might be obtained by repeated applications of pressure, alternating with relief, using a gas soluble in the cooking liquor, it being then possible to reduce thus the partial pressure of inert gas to the same value as by evacuation; the residual gas would dissolve in the cooking acid and thus facilitate penetration. Sulphur dioxide was the obvious choice for such a purpose.

For these experiments, the modifications shown below were made in the apparatus. The manometer was a simple horizontal capillary manometer, merely a length of capillary tubing sealed at one end and containing a column of air sealed off by a mercury thread. Thus the length of the air column varied inversely as the pressure.



Sulphur dioxide gas pressure was applied by opening valve (2) with the rest of the system closed. After ten minutes, valve (2) was closed, valve (1) opened and the pressure allowed to fall to atmospheric. A few minutes were allowed for desorption to take place. Valve (1) was then closed and the procedure repeated until the desired partial pressure of air (calculated to be less than the critical pressure mentioned above) was reached. After this pre-treatment, the rest of the cooking procedure was as usual.

It might be well to point out that the above procedure in no way corresponds to a flow of sulphur dioxide gas through the cell. Such a flow would not remove, within a reasonable time, the air entrapped in the fibre cavities when chips of ordinary size are used.

Run #166

Wood - Black Spruce heartwood
    Chip length - 3/4"
    Density - 0.34
    Moisture - 9.0%
Cooking liquor - Total sulphur dioxide - 5.36%
    Free - 4.01
    Combined - 1.35
Pressure - 7 atmospheres.
Temperature - up to 140°C. in $1^{h}00'$
    kept at 140°C. for $3^{h}00'$

Sulphur dioxide gas pressure slightly greater than 2 atmospheres was applied to the chips six times.

Calculated partial pressure of residual air - abt. 1.3 cm. of Hg.

The chips were very soft, very uniformly cooked, and there was no indication of burning.

Mullen Burst Ratio - 155.5%
Lignin in pulp - 3.6%
Yield of pulp - 52.2%
Yield of cellulose - 50.3%
Residual lignin - 1.9%

Run #167

Same as Run #166 except

Cooking liquor -	Total sulphur dioxide	- 3.87%
	Free	- 2.52
	Combined	- 1.35

Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h30'$

The chips were extremely soft, and there were no signs of burning.

Mullen Burst Ratio - 120.5%
Lignin in pulp - 3.4%
Yield of pulp - 46.9%
Yield of cellulose - 45.3%
Residual lignin - 1.6%

In spite of the small difference in lignin contents of pulps #166 and 167, pulp #167 seemed much more cooked than pulp #166.

A calculation, based on the volume of the cell and the assumption that the chips would adsorb about 5% of their weight of sulphur dioxide[32], indicated that the effect of the sulphur dioxide pre-treatment would be to raise the final concentration of free sulphur dioxide in the cooking liquor by about 0.8%.

Consequently, the following run, originally made for another purpose, should give some idea of the relative effects of the pre-treatment procedures, evacuation and sulphur dioxide gas treatment, on comparison with Run #166.

Run #171

Cooking liquor - Total sulphur dioxide - 6.42%
Free - 5.10
Combined - 1.32
Pressure - 10 atmospheres
The cell was evacuated 30' at 1 cm. of Hg.

Other conditions same as in Run#166.

Mullen Burst Ratio - 139%
Lignin in pulp - 2.7%
Yield of pulp - 50.3%
Yield of cellulose - 48.9%
Residual lignin - 1.4%

Since the pulp from this cook had been slightly overcooked in comparison to that from Run #166, the differences are those expected, and, lacking further comparisons, it appears at first sight that the two methods of pre-treatment produce much the same result.

A procedure such as the above does not appear to have been used before. The nearest approach is given by a patent[33] covering a process involving subjecting the chips to a vacuum, then introducing gaseous sulphur dioxide, after which an alkaline cooking liquor, such as sodium hydroxide, is supplied. The result, however, would obviously closely resemble a neutral sulphite cook, or even something intermediate between a soda cook and a neutral sulphite cook.

In the following run, an attempt was made to carry out a cook on a larger scale under conditions approaching as nearly as possible those of Run #166.

Run #A3

Made in two-litre bomb.

Wood - Black Spruce, low density.
Average chip length - 7/8"
Moisture - 10.5%

Cooking liquor -	Total sulphur dioxide	- 5.40%
	Free	- 4.10
	Combined	- 1.30

Temperature - up to 140°C. in $1^h15'$
kept at 140°C. for $2^h30'$

The bomb was subjected to sulphur dioxide gas pressure of 15 lbs./sq.in., allowed to stand 10', the pressure relieved to atmospheric, and the bomb allowed to stand 5'. This procedure was repeated 5 times. The bomb was then attached to the reservoir of the small scale apparatus, liquor forced in and the pressure kept constant throughout the cook at 90 lbs./sq.in. No relief was used.

The bulk of the chips were treated in the mill by the usual procedure. A few representative chips were treated by the small scale procedure.

Mullen Burst Ratio of pulp treated in mill - 109.5%
Mullen Burst Ratio of pulp treated in lab. - 133%

Lignin in pulp - 3.8%

Yield of screenings - 0.8%
Pulp was lost during screening, hence the yield was not determined.

Run #A4

Same as Run #A3, but bomb not connected to liquor reservoir. The pressure was allowed to rise to 90 lbs. per sq.in. and kept constant by relief. Also

Cooking liquor -	Total sulphur dioxide	- 4.30%
	Free	- 2.95
	Combined	- 1.35

Mullen Burst Ratio of pulp treated in mill - 90%
Mullen Burst Ratio of pulp treated in lab. - 121%

Lignin in pulp - 4.6%

The runs on this larger scale confirm quite well the small scale results. The sulphur dioxide pre-treatment again completely eliminated burning in spite of the rapid rise of temperature.

Work was begun on the application of this procedure to a one cubic foot digester equipped with a liquor circulating pump and indirect heating. Unfortunately, considerable difficulties were experienced due to defects in the apparatus, chiefly pump leakage. A few exploratory runs gave encouraging results inasmuch as the sulphur dioxide gas pre-treatment completely eliminated burning, although the temperature of the cooking liquor was raised to 140°C. in $1^h15'$. The set-up is being completely overhauled, and it is hoped to continue work on this scale in the near future.

It is regretted that time was not available to investigate various combinations of evacuation with sulphur dioxide injection as methods of pre-treatment, since this appears to promise interesting possibilities from a practical standpoint. This is especially desirable since any attempt to apply this procedure on a commercial scale would most likely involve the use of relief gases, which usually are composed of only 80% sulphur dioxide.

Influence of preliminary evacuation in long cooks

At first sight, it appeared that the abnormally high strength of the pulps obtained by the shortened cooking procedure with evacuation might be directly connected with the evacuation itself. An attempt was made to study this point.

Run #99

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.41
Moisture - 8.4%
Cooking liquor - Total sulphur dioxide - 5.00%
Free - 3.65
Combined - 1.35
Pressure - varied so as to be always slightly higher than the vapour pressure of the liquor, up to a maximum of 6 atmospheres (reached at 120°C.), then held constant at 6 atm.
Temperature - up to 110°C. in $1^{h}30'$)
kept at 110°C. for $1^{h}30'$)
from 110 to 140°C. in $1^{h}00'$)
kept at 140°C. for $4^{h}30'$) $8^{h}30'$

The cell was not evacuated previous to introduction of the liquor

Liquor ratio - approximately 7.5 cc./gm. of wood (instead of the usual value of about 10 cc./gm. of wood).

The chips were soft but very slightly burned in centre.

Mullen Burst Ratio - 120%
Lignin in pulp - 8.5%
Yield of pulp - 52.3%
Yield of cellulose - 47.9%
Residual lignin - 4.4%

Run #100

Same as Run #99 except that the pressure was kept constant at 6 atmospheres throughout the cook.

The chips were very soft, and there was no burning.

Mullen Burst Ratio - 136.5%
Lignin in pulp - 2.7%
Yield of pulp - 49.1%
Yield of cellulose - 47.8%
Residual lignin - 1.3%

Run #101

Same as Run #100, but the cell was evacuated 30' at 1 cm. of Hg.

The chips were very soft, and there was no burning.

Mullen Burst Ratio - 124%
Lignin in pulp - 1.5%
Yield of pulp - 48.1%
Yield of cellulose - 47.4%
Residual lignin - 0.7%

These runs should be compared to one where the wood is cooked by the shortened procedure with preliminary evacuation, as below -

Run #94

Same as Run #101 except
Temperature - up to 140°C. in $1^h15'$
kept at 140°C. for $3^h30'$

The chips were well cooked, with only faint indication of burning.

Mullen Burst Ratio - 156.5%
Lignin in pulp - 5.7%
Yield of pulp - 53.0%
Yield of cellulose - 50.0%
Residual lignin - 3.0%

Run #99 was carried out under conditions parallelling as much as possible mill operation, except for higher liquor ratio and absence of gaseous relief. There was very slight burning, just enough to make the centres of the chips a little hard, causing raw pulp and high screenings. Still, the bursting strength was distinctly above normal sulphite pulp strength.

Run #100 showed clearly the advantage of maintaining a high pressure throughout the cook by application of hydrostatic pressure in preference to allowing the pressure to build up from the vapour pressure of the cooking liquor. This makes for more rapid and more complete penetration and hence for better cooking.

Run #101 showed that evacuation <u>per se</u> does <u>not</u> increase the bursting strength. The higher strength is obtained only when advantage is taken of the effect of evacuation in accelerating penetration and thus allowing faster cooking, as shown by Run #94.

This, and the fact that the application of high gas pressure throughout the cook is almost as effective as pre-evacuation, is further evidence against the hypothesis that higher pulp strengths are obtained with pre-evacuation because of the elimination of sulphuric acid formation.

The pulps obtained from Runs #100 and #101 are clearly overcooked and the strength and yield are therefore lower than could be obtained with shorter cooking time. The constancy of the cellulose yield in Runs #99, 100 and 101 is, however, quite striking.

The lower strength of pulp #101 compared to that of pulp #100 is to be explained by the greater delignification. Penetration being more rapid, the liquor acts on the cellulose for a longer time, even though at low temperature, and slightly more degradation occurs, as shown by the very slightly reduced cellulose yield.

Influence of Moisture Content

Having established conditions for the pretreatment of wood for furthering rapid penetration, a number of other factors were investigated. The first of these, the influence of the moisture content of the wood, has been the subject of numerous investigations. As it has been found that the moisture content of the wood affects the temperature schedule which must be followed in the early stages of the cook to avoid burning, the pre-treatment mentioned above, which controls burning, made it well worth while repeating the investigations with the new temperature schedule developed.

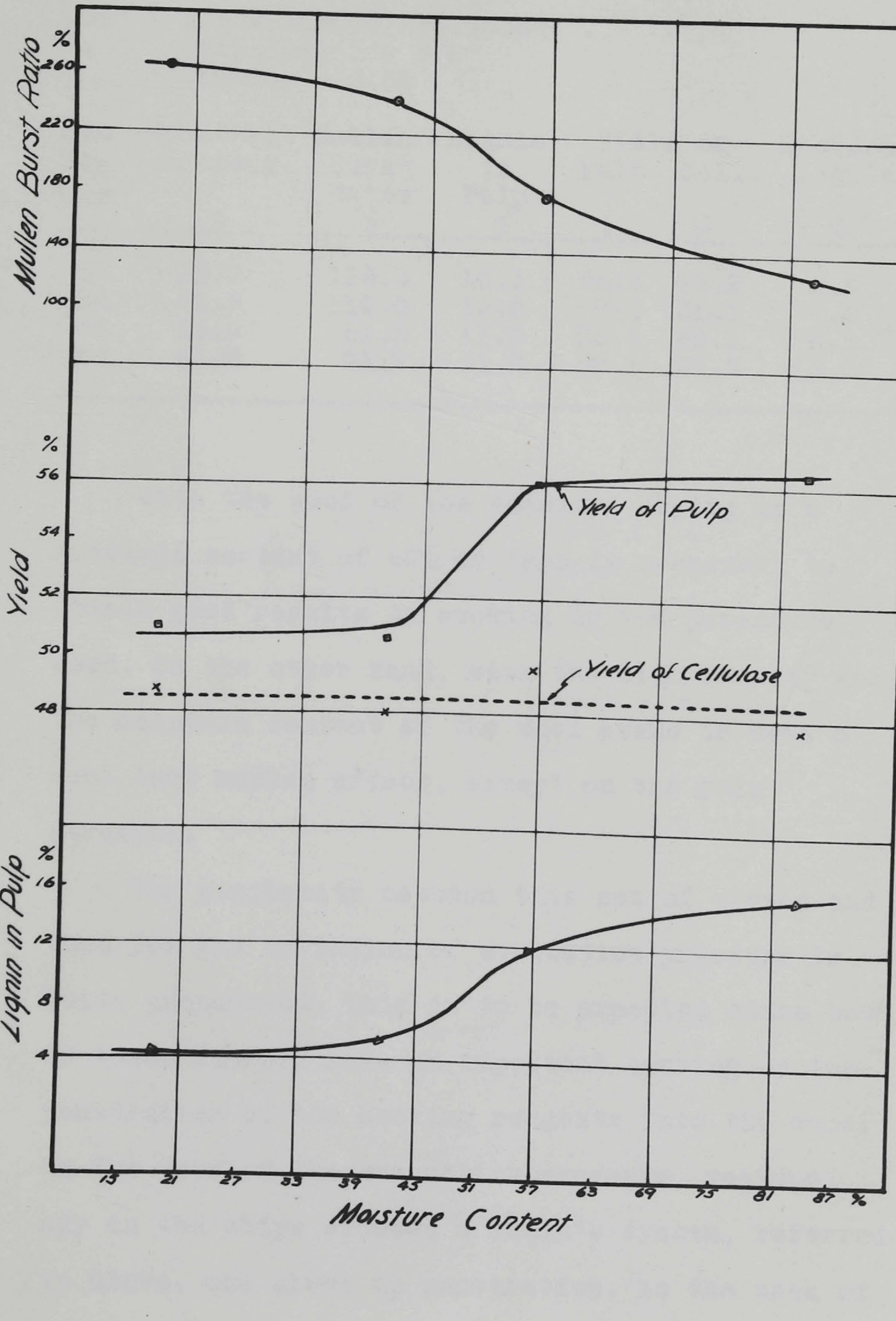
The moisture content of the samples in this group of runs was adjusted by soaking the chips overnight in water, after preliminary evacuation, and then drying them in an oven at 70°C. until the desired moisture content was reached. The values of moisture content reported are on the basis of the bone-dry weight of wood.

Runs #78 - 81 (Figure 9.)

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.31
Cooking liquor - Total sulphur dioxide - 5.00%
Free - 3.65
Combined - 1.35
Pressure - 7 atmospheres
Temperature - up to 140°C in $1^h00'$
kept at 140°C. for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Moisture Content %	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
80	18.4	265.5	4.6	51.0	48.8	2.2
79	41.2	242.5	5.4	50.6	48.0	2.6
81	56.3	178	11.7	56.0	49.5	6.5
78	83.4	124	15.5	56.4	47.6	8.8

Figure 9.


%
260
220
180
140
100
Mullen Burst Ratio
%
56
54
52
50
48
Yield
Yield of Pulp
Yield of Cellulose
%
16
12
8
4
Lignin in Pulp
15
21
27
33
39
45
51
57
63
69
75
81
87
%
Moisture Content

Runs #83 - 87 (Figure 10.)

Same as Runs #78 - 81 except

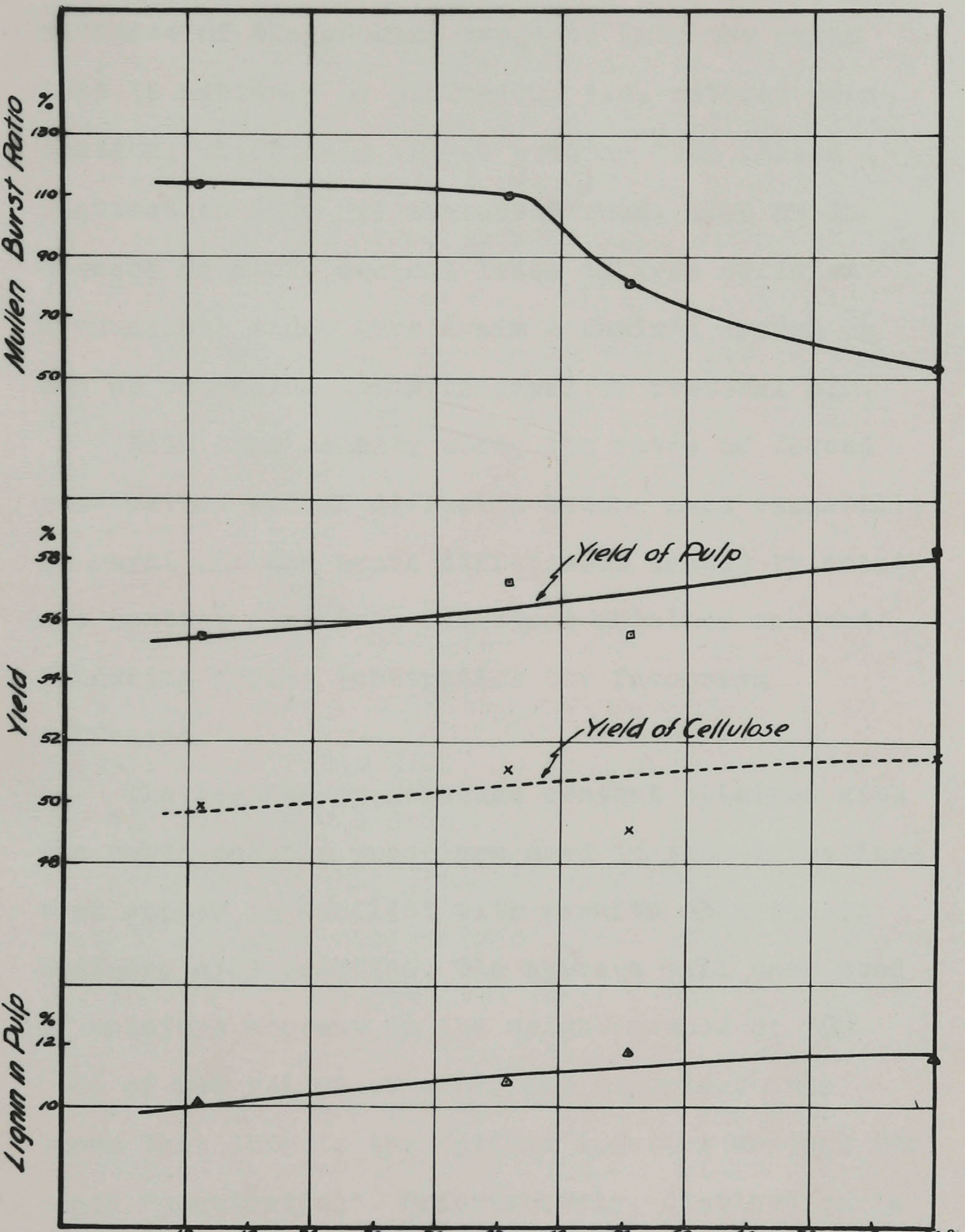
Wood - Black Spruce heartwood
Chip length - 3/8"
Density - 0.52

Run No.	Moisture Content %	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residua Lignin %
87	13.2	113.5	10.1	55.5	49.9	5.6
84	42.9	110.0	10.8	57.3	51.1	6.2
86	54.5	81.2	11.8	55.6	49.1	6.5
83	84.0	52.7	11.6	58.3	51.5	6.8

With the wood of low density, drying to a moisture content of 40% or less is necessary to obtain good results on cooking by the procedure used. On the other hand, with the high density wooc the moisture content of the wood seems to have a much less marked effect, except on the pulp strength.

The similarity between this set of curves and that for the variation of evacuation pressure is quite pronounced. This is to be expected since botl of these factors have an important bearing on the penetration of the cooking reagents into the wood. In the case of the evacuation pressure, residual air in the chips creates a Jamin's system, referrec to above, and slows up penetration. In the case of

Figure 10.


Mullen Burst Ratio
%
130
110
90
70
50
Yield
%
58
56
54
52
50
48
Yield of Pulp
Yield of Cellulose
Lignin in Pulp
%
12
10
12
18
24
30
36
42
48
54
60
66
72
78
84 %
Moisture Content

the moisture content, an increasing amount of moisture means that an increasing part of the entrance of the cooking reagents into the chips must be achieved by diffusion, i.e. natural penetration, which is a slower process than forced penetration into dry evacuated wood. Also an increased moisture content leads to less efficient evacuation, since here again a Jamin's system is set up retarding the withdrawal of residual air.

With high density wood, the rates of forced penetration and of diffusion become more comparable in magnitude and hence differences caused by moisture content diminish, increased moisture content hindering forced penetration but favouring diffusion.

The results on moisture content obtained with the rapid cooking procedure used in this investigation appear to conflict with results obtained in ordinary mill practice. The average mill uses wood of moisture content in the neighbourhood of 70% (40% of wet weight of wood) and experience has shown that this is the optimum moisture content for rapid "penetration". Unfortunately, distinction is seldom made between forced penetration and diffusion. Under the conditions of an industrial cook, where the chips submerged in the cooking liquor are filled with air, and this air is expanding as the temperature rises, an appreciable moisture content is necessary to assist the entrance of the cooking reagents into the wood by diffusion, since forced penetration under those conditions is very slow. This accounts for the apparent disagreement of the results.

With the rapid temperature rise used in the present work, however, the importance of the diffusion factor is reduced, and the differences observed are more largely due to true forced penetration phenomena.

Hrubesky and Chidester[30] have shown that moist wood burns more quickly than oven-dried wood, although they claim that the rate of penetration is only slightly reduced.

Concerning pulp quality, moisture content appears to be of small moment under the usual cooking conditions using a slow temperature rise and no evacuation. Hägglund[34] found that the moisture content of the wood affected the pulp strength only slightly, the results rather favouring the moister wood. Richter[35] reported that wood which had been air-dried a year gave better quality and more easily bleached pulp than wood which had stood in water for a year.

Influence of maximum cooking temperature

The object of this group of runs was to compare the effect of different maximum temperatures, when cooking down to pulps of the same lignin content with the new cooking procedure and temperature schedule.

The temperature schedule used in this group of runs is that used practically throughout the investigation; it is of the "flat curve" type, viz. a steep rise to maximum temperature followed by a constant temperature to the end of the cook.

It was not thought worth while at this time to study various temperature schedules, since much work has already been done along that line by Miller and Swanson[20, 36, 37], Monnberg[38, 39], and others[40].

Run #56

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.36
Moisture - 6.4%
Cooking liquor - Total sulphur dioxide - 5.00%
Free - 3.65
Combined - 1.35
Pressure - 7 atmospheres
Temperature - up to 140°C. in 1^{h}00'
kept at 140°C. for 3^{h}00'
The cell was evacuated 30' at 1 cm. of Hg.

Mullen Burst Ratio - 187%
Lignin in pulp - 4.0%
Yield of pulp - 50.6%
Yield of cellulose - 48.6%
Residual lignin - 2.0%

Run #68

Same conditions as in Run #56 except

Temperature - up to 130°C. in 55'
kept at 130°C. for 5ʰ05'

Mullen Burst Ratio - 186.5%
Lignin in pulp - 5.2%
Yield of pulp - 57.0%

Run #71

Same as Run #68 except

Temperature - kept at 130°C. for 6ʰ05'

Mullen Burst Ratio - 193.5%
Lignin in pulp - 3.2%
Yield of pulp - 52.4%

Assuming linear variation of Mullen burst ratio and yield with lignin content of the pulp, which is sufficiently accurate within narrow limits, we get, by interpolation -

Lignin in pulp - 4.0%
Time at Maximum Temperature - 5ʰ40'
Mullen Burst Ratio - 190.5%
Yield of pulp - 54.0%
Yield of cellulose - 51.8%
Residual Lignin - 2.2%

Run #69

Same conditions as in Run #56 except

Temperature - up to 150°C. in 1ʰ05'
kept at 150°C for 2ʰ10'

Mullen Burst Ratio - 180.5%
Lignin in pulp - 6.0%
Yield of pulp - 52.4%

Run #70

Same as Run #69 except

Temperature - kept at 150°C. for $2^h40'$

Mullen Burst Ratio - 165%
Lignin in pulp - 3.0%
Yield of pulp - 46.8%

Again interpolating, we get

Lignin in pulp - 4.0%
Time at Maximum Temperature - $2^h30'$
Mullen Burst Ratio - 170%
Yield of pulp - 48.7%
Yield of cellulose - 46.8%
Residual lignin - 1.9%

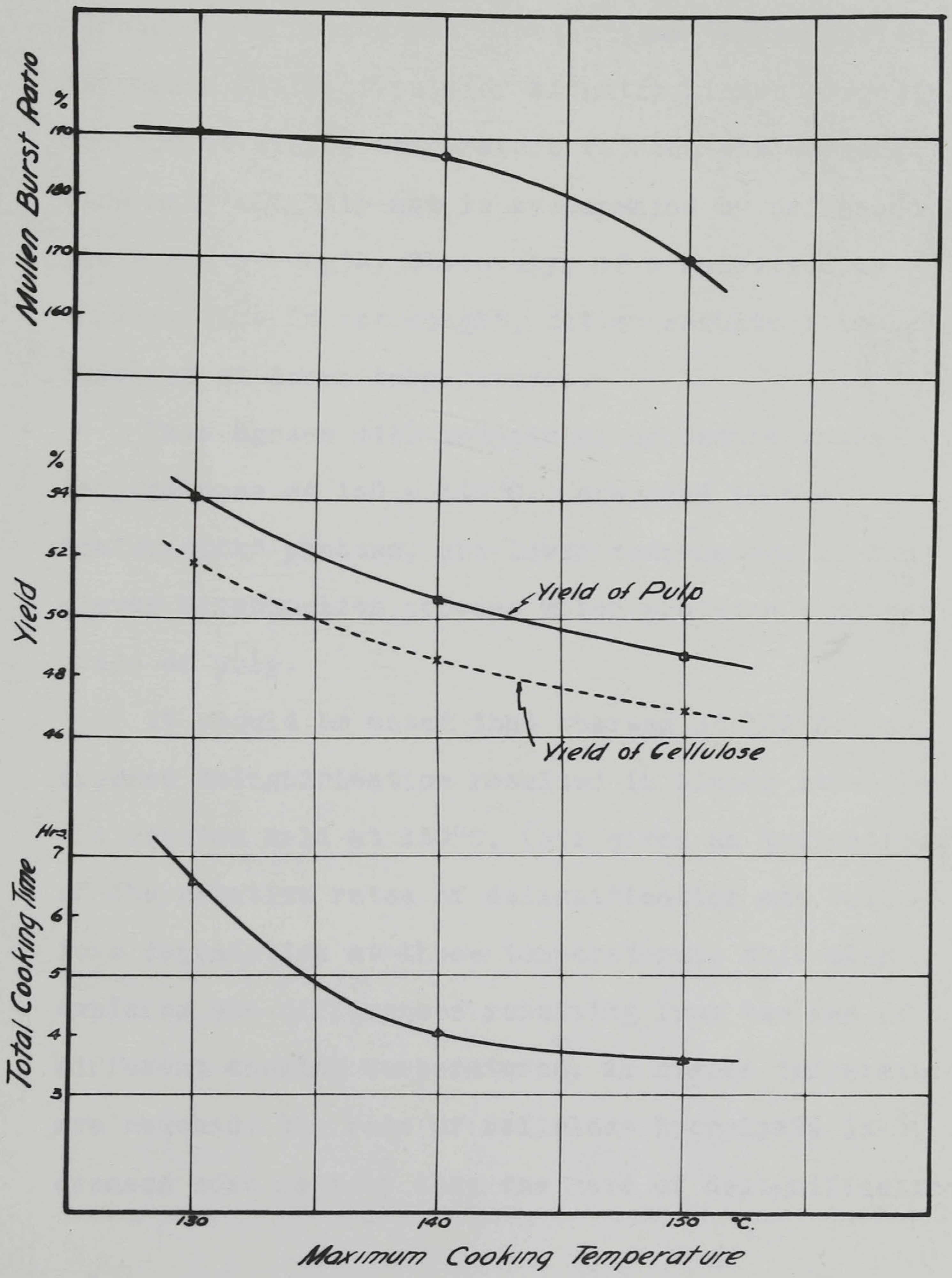
Summarizing - (Figure 11.)

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.36
Moisture - 6.4%
Cooking liquor - Total sulphur dioxide - 5.00%
Free - 3.65
Combined - 1.35
Pressure - 7 atmospheres
The cell was evacuated 30' at 1 cm. of Hg.

Lignin in pulp - 4.0% in all cooks.

Run No.	Maximum Temp. °C.	Total Cooking Time	Mullen Burst Ratio %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
68 71	130	$6^h35'$	190.5	54.0	51.8	2.2
56	140	$4^h00'$	187	50.6	48.6	2.0
69 70	150	$3^h35'$	170	48.7	46.8	1.9

Figure 11.


Mullen Burst Ratio
%
190
180
170
160
Yield
%
54
52
50
48
46
Yield of Pulp
Yield of Cellulose
Total Cooking Time
Hrs.
7
6
5
4
3
130
140
150
°C.
Maximum Cooking Temperature

From a practical point of view, 140°C. is the optimum cooking temperature. Cooking at lower temperature requires a much longer time though giving increased yield of pulp of slightly higher strength. Cooking at higher temperature reduces the cooking time only slightly and is accompanied by decreased yield and strength. Obviously, if a reduction in cooking time is not sought, better results will be obtained at lower temperatures.

This agrees with industrial procedure where temperatures of 140 - 145°C. are used in the "quick-cook" process, and lower temperature in the slower Mitscherlich process which produces a better grade of pulp.

It should be noted that whereas at 130°C. increased delignification resulted in higher strength, the reverse held at 150°C. This gives an indication of the relative rates of delignification and cellulose degradation at those temperatures; this also explains the differences resulting from the use of different cooking temperatures. As higher temperatures are reached, the rate of cellulose hydrolysis increases more rapidly than the rate of delignification.

Influence of exposed surface of chips

In the procedure adopted in the work, the exposed surface of the chips was less than in usual practice, and it was thought possible that this factor might influence the strength of the pulps made. For this reason, the chip size was varied in the following group of runs.

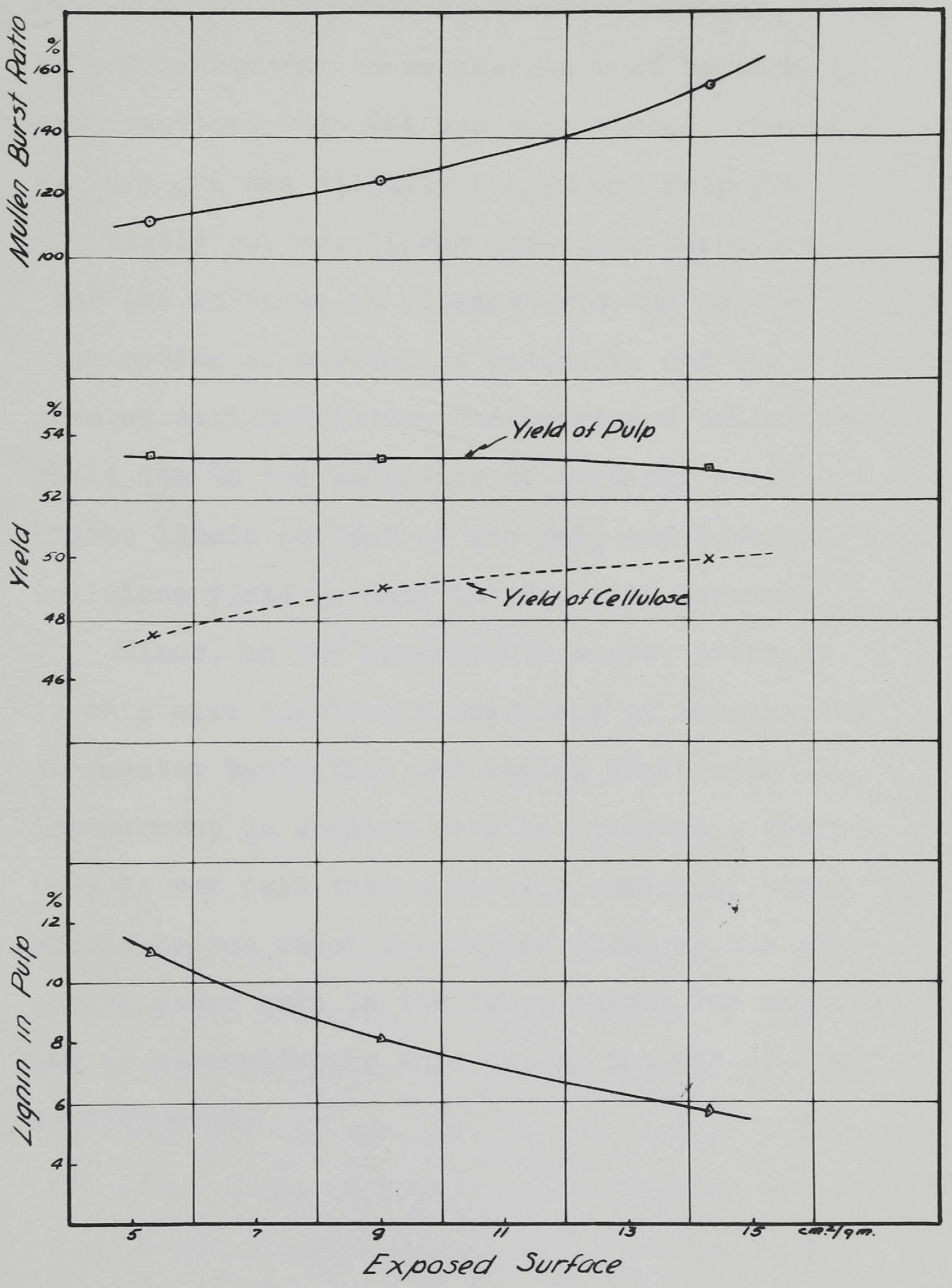
The samples were all of the same length along the fibre direction and of the same weight. Varying numbers of blocks of the same shape were cut from the sample for each run and sandpapered down to dimensions predetermined so as to obtain the desired exposed surface.

Runs #94 - 96 (Figure 12.)

Wood - Black Spruce heartwood
Chip length - 2.0 cm.
Density - 0.41
Moisture - 8.4%
Cooking liquor - Total sulphur dioxide - 5.00%
Free - 3.65
Combined - 1.35
Pressure - 7 atmospheres
Temperature - up to 140°C. in $1^h15'$
kept at 140°C. for $3^h30'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Exposed Surface cm^2/gm.	Mullen Burst Ratio	Lignin in Pulp	Yield of		Residual Lignin
		%	%	Pulp %	Cell. %	%
95	5.3	112	11.0	53.4	47.5	5.9
96	9.0	126	8.1	53.3	49.0	4.3
94	14.3	156.5	5.7	53.0	50.0	3.0

Figure 12.


Mullen Burst Ratio
%
160
140
120
100
Yield
%
54
52
50
48
46
Yield of Pulp
Yield of Cellulose
Lignin in Pulp
%
12
10
8
6
4
5
7
9
11
13
15
cm.²/gm.
Exposed Surface

The decrease in chip size resulted in markedly improved cooking results. However, interpretation of these results must be done with caution. Pulp #94 was well cooked, whereas Pulp #96 was slightly burned and Pulp #95 distinctly burned. It was possible, therefore, that the increase in strength was due to the elimination of screenings entirely, and the greater delignification and increased cellulose yield due to the reduction of burning, since higher lignin content of the pulp and lowered cellulose yield go hand in hand with burning.

Since, in the experiments above, decrease in chip size involved elimination of burning due to greater tangential and radial penetration, improvement in cooking results followed . Therefore it was felt that a similar series of cooks should be run under conditions where no burning should occur even in the large chips. The simplest way of accomplishing this was by the use of lower density wood.

<u>Runs #235 - 238</u> (Figure 13.)

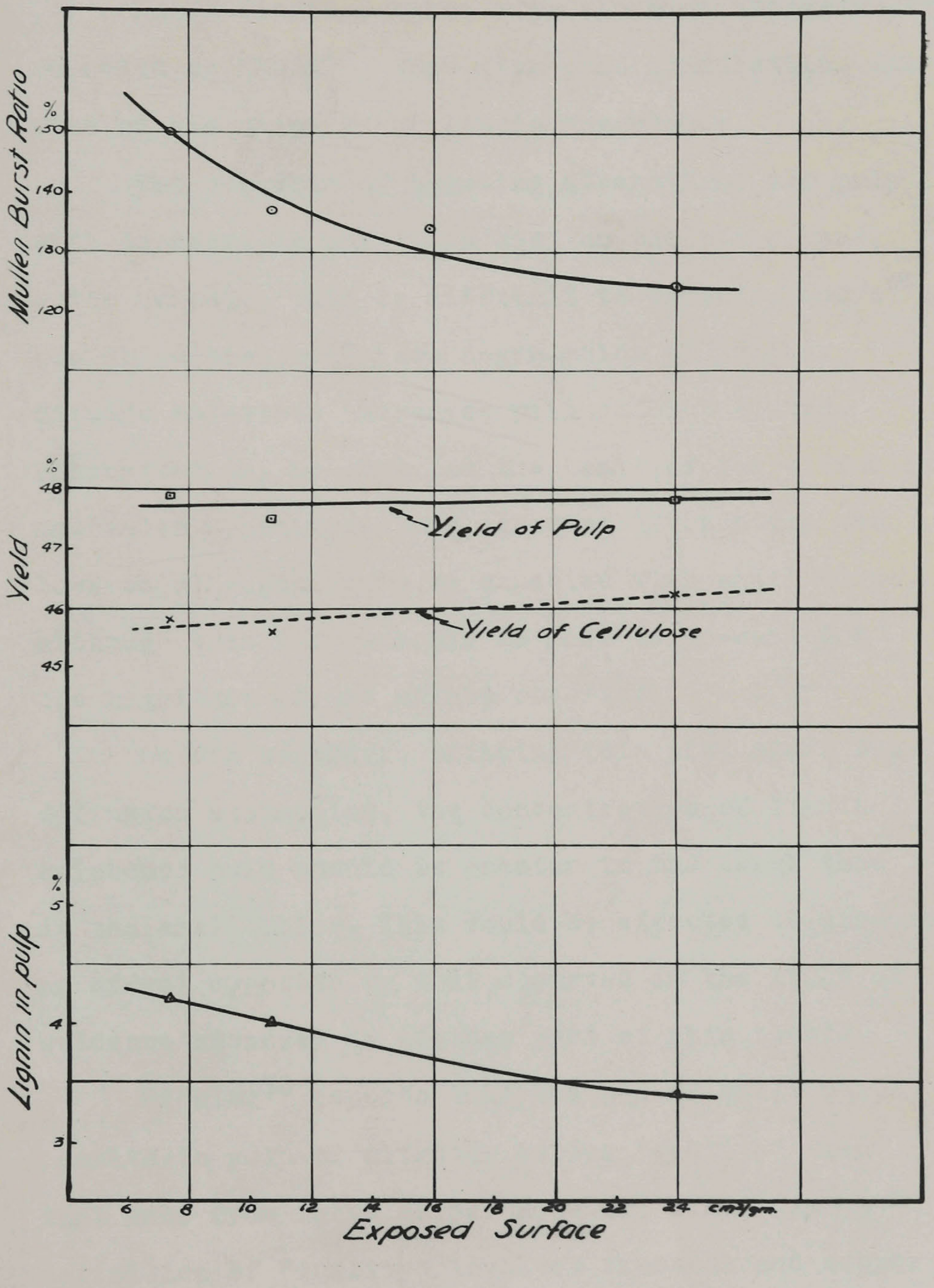
Wood - Black Spruce heartwood
Chip length - 2.0 cm.
Density - 0.34
Moisture - 9.0%
Cooking liquor - Total sulphur dioxide - 5.24%
Free - 3.89
Combined - 1.35
Pressure - 10 atmospheres
Temperature - up to 140°C. in 1^{h}00'
kept at 140°C. for 3^{h}00'
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Exposed Surface cm^2/gm.	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
235	7.4	150	4.2	47.9	45.8	2.1
237	10.7	137	4.0	47.5	45.6	1.9
238x	15.9	134	---	----	----	---
236	24.0	124	3.4	47.8	46.2	1.6

x - Temperature dropped during cook, hence slightly higher strength

In this case, where satisfactory cooking was obtained with all sizes of chips, it is seen that an increase in exposed surface produced only very slightly greater delignification. The small differences observed are probably to be explained on the basis of the diffusion of sulphur dioxide into the impregnated chips; there is a greater sulphur dioxide concentration gradient in the case of the large chips, resulting in lower sulphur dioxide concentration in the interior of the chips and in reduced delignification.

Figure 13.



Mullen Burst Ratio
%
150
140
130
120
Yield
%
48
47
46
45
Yield of Pulp
Yield of Cellulose
Lignin in pulp
%
5
4
3
6
8
10
12
14
16
18
20
22
24
cm²/gm.
Exposed Surface

The yield was independent of the size of the chips.

These findings agree with those of Stangeland[41], reported by Klein[42], that with good circulation, the size of the chips is of little importance.

The decrease of bursting strength of the pulp with decrease in chip size was, on the other hand, quite marked. This is difficult to explain. Moore[43] has shown that cellulose degradation by sulphur dioxide solutions increases with sulphur dioxide concentration. So that, on the basis of the diffusion mechanism mentioned above, greater degradation and lowered strength could be expected with small chips, although this can scarcely be made to account for the magnitude of the effect observed.

On the contrary, bringing into play again the diffusion assumption, the concentration of lignin sulphonic acid should be greater in the large than in the small chips. This would be expected to produce an effect opposite to that observed in the light of evidence advanced in another part of this thesis.

Richter[35] reports that the use of small chips results in pulp of slightly better "quality" than that made from large chips. However, since his definition of "quality" involves freeness and copper number as well as bursting strength, and since no bursting strength values are given, no comparison can be made.

Attempts have been made in many mills to pulp groundwood tailings by the sulphite process. The results are still undecisive but indicate poorer strength and lower yield than with chips.

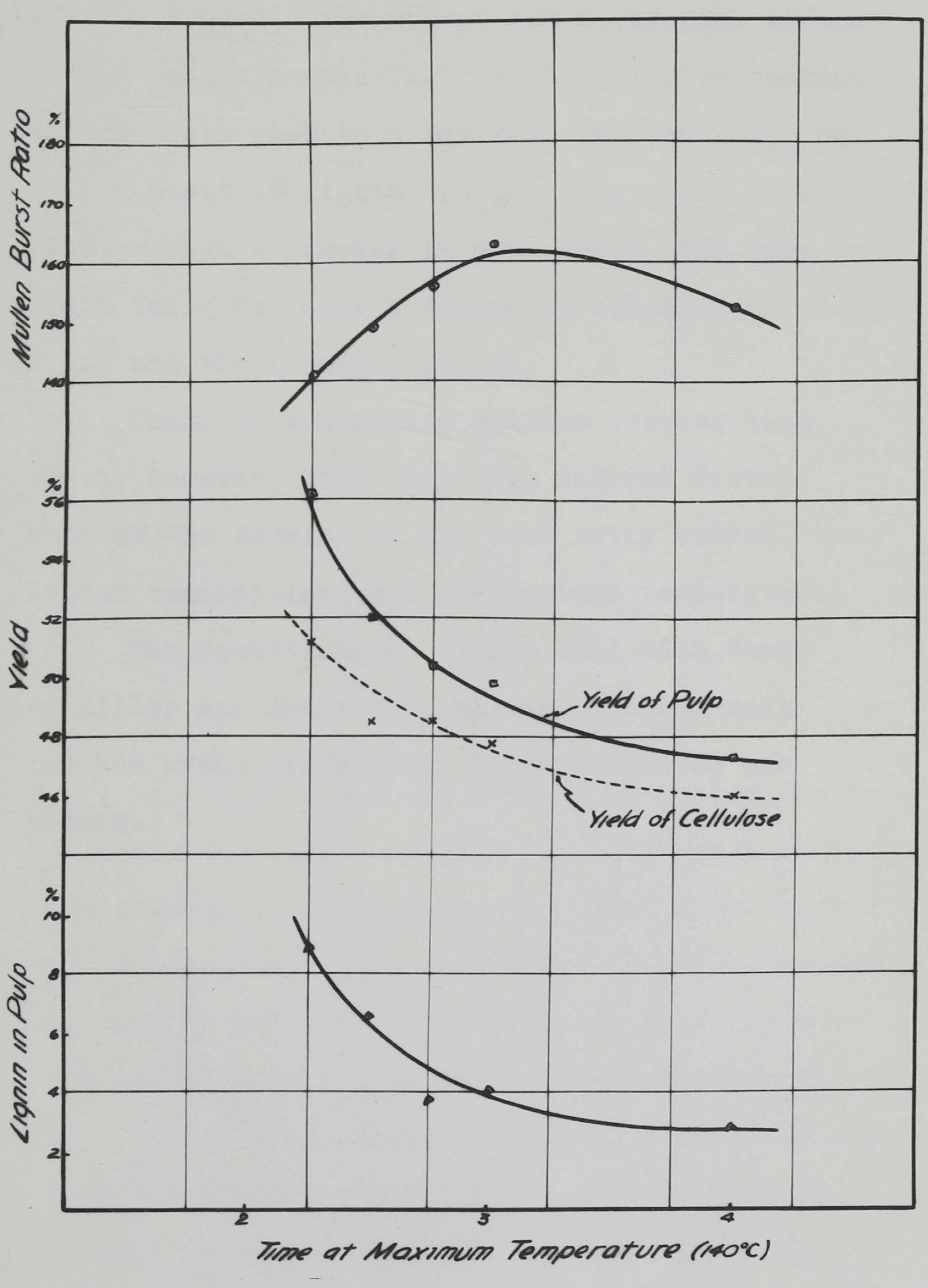
Influence of cooking time at maximum temperature

Runs #137 - 144 (Figure 14.)

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.42
Moisture - 10.3%
Cooking liquor - Total sulphur dioxide - 4.75%
Free - 3.45
Combined - 1.30
Pressure - 7 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for time specified below.
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Time at Max.Temp.	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
142	$2^h15'$	141	8.9	56.2	51.2	5.0
141 143	$2^h30'$	149	6.6	52.0	48.5	3.5
144	$2^h45'$	156	3.8	50.4	48.5	1.9
137 138	$3^h00'$	163	4.1	49.8	47.8	2.0
140	$4^h00'$	152.5	2.8	47.3	46.0	1.3

Figure 14.


Mullen Burst Ratio
%
180
170
160
150
140
Yield
%
56
54
52
50
48
46
Yield of Pulp
Yield of Cellulose
Lignin in Pulp
%
10
8
6
4
2
2
3
4
Time at Maximum Temperature (140°C)

The pulp from Run #142 was raw; although there were few shieves, the fibres were hard and stiff and good strength was not developed. As the fibres became increasingly soft on longer cooking, the strength rose to a maximum when the pulp contained about 4% lignin. Beyond this point, the rate of lignin removal is much lower, the drop in yield being due more and more to cellulose hydrolysis and the strength falls.

There is a definite optimum cooking time, which, however, will vary with several factors such as the density of the wood being cooked, the liquor composition, and the maximum temperature.

The results agree fairly well with those of Miller and Swanson[21], allowance being made for the great differences in experimental procedure.

Influence of liquor composition

(a) Free sulphur dioxide concentration

Runs #168 - 172 (Figure 15.)

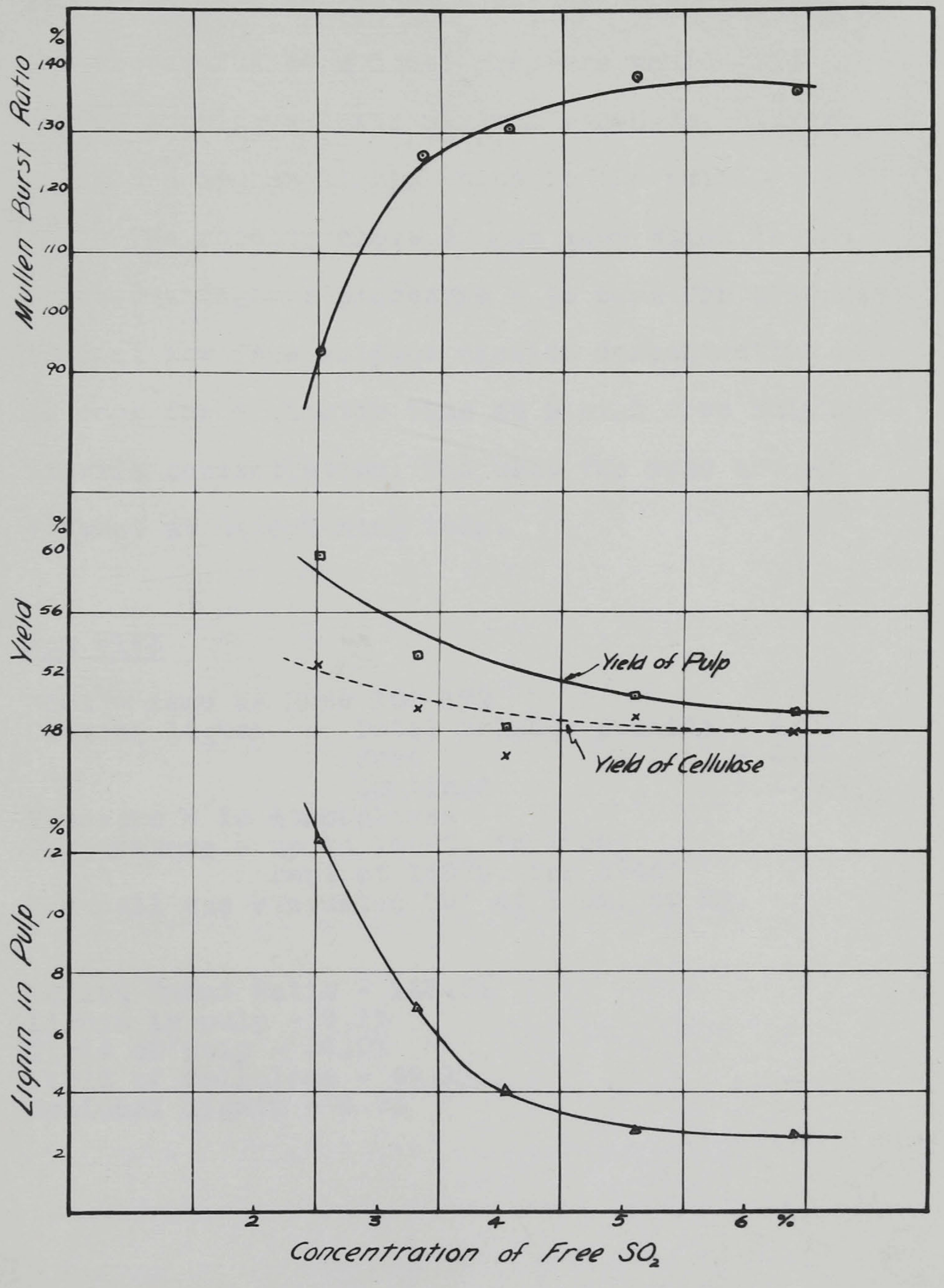
Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.34
Moisture - 9.0%
Cooking liquor - Combined sulphur dioxide - 1.32%
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Free SO_2 %	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
168	2.52	93.5	12.4	59.9	52.5	7.4
171	3.33	126	6.8	53.1	49.5	3.6
169	4.05	130.5	4.0	48.3	46.4	1.9
172	5.10	139	2.7	50.3	48.9	1.4
170	6.40	135.5	2.6	49.2	47.9	1.3

In Run#170 gas evolution from the liquor was observed just before maximum cooking temperature was reached. In the cooks with lower free sulphur dioxide concentration, there was no gas evolution. It will be noticed that the curves approach the horizontal at the point where gas evolution begins.

In this connection, it must be borne in mind that the maximum concentration of free sulphur dioxide which can be maintained in the liquor

Figure 15.


%
140
130
120
110
100
90
Mullen Burst Ratio
%
60
56
52
48
Yield
Yield of Pulp
Yield of Cellulose
%
12
10
8
6
4
2
Lignin in Pulp
2
3
4
5
6
%
Concentration of Free SO_2

once a given cooking temperature has been reached is solely dependent on the pressure maintained. Thu it can be predicted that a series of cooks, such as the above, run at a lower pressure would give curves showing a lower maximum strength, higher yield and higher lignin value in the pulp.

The results above do not show which is the more advantageous procedure - to cook for a longer time at low free sulphur dioxide concentration or to cook for a shorter time at a high free sulphur dioxide concentration. The next two runs are an attempt at determining this.

Run #173

Wood - same as Runs 168-172

Cooking liquor -	Total sulphur dioxide	- 4.01%
	Free	- 2.69
	Combined	- 1.32

Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h45'$
The cell was evacuated 30' at 1 cm. of Hg.

Mullen Burst Ratio - 128.5%
Lignin in pulp - 9.1%
Yield of pulp - 54.0%
Yield of cellulose - 49.1%
Residual lignin - 4.9%

Run #174

Same as Run #173 except

Cooking liquor - Total sulphur dioxide - 8.35%
Free - 7.03
Combined - 1.32
Temperature - kept at 140°C. for $2^h00'$

Mullen Burst Ratio - 165%
Lignin in pulp - 6.7%
Yield of pulp - 52.4%
Yield of cellulose - 48.9%
Residual lignin - 3.5%

Clearly, the use of higher free sulphur dioxide concentration results in much higher strength and greatly reduced cooking time. The yields are practically the same, allowing for the difference in lignin content of the pulps. Adjustment of the duration of the cook to produce pulps of the same lignin content would further increase the difference in cooking time and would be expected to further increase the difference in pulp strengths.

Obviously, advantage can be taken of this effect only by the use of high pressure to prevent, or at least to reduce, gas evolution from the liquor. The initial concentration of the liquor will have little effect if the digester pressure is maintained at such a low level that much gas is relieved as the cooking temperature is reached.

It is to be expected that the effect of variations in free sulphur dioxide concentration will be affected by the chip size. A concentration gradient from the outside to the inside of the chip is set up due to diffusion, and this will tend to reduce the effect of varying liquor concentration. Consequently, reducing the chip size should bring out greater differences on changing the free sulphur dioxide concentration.

Runs #239 and 240

Wood - Black Spruce heartwood
Chip length - 2.0 mm.
Density - 0.54
Moisture - 8.3%
Cooking liquor - Combined sulphur dioxide - 1.35%
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $2^h45'$
The cell was evacuated at 1 cm. of Hg.

Run No.	Free SO_2 %	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
239	3.89	92.5	12.4	54.2	47.5	6.7
240	6.95	108.5	2.0	43.7	42.8	0.9

By comparison of these two runs with Runs #169 and 170, it is evident that reduction in chip length makes much more obvious the effect of increased free sulphur dioxide concentration, in all probability by reduction of the concentration gradient.

Influence of liquor composition

(b) Combined sulphur dioxide

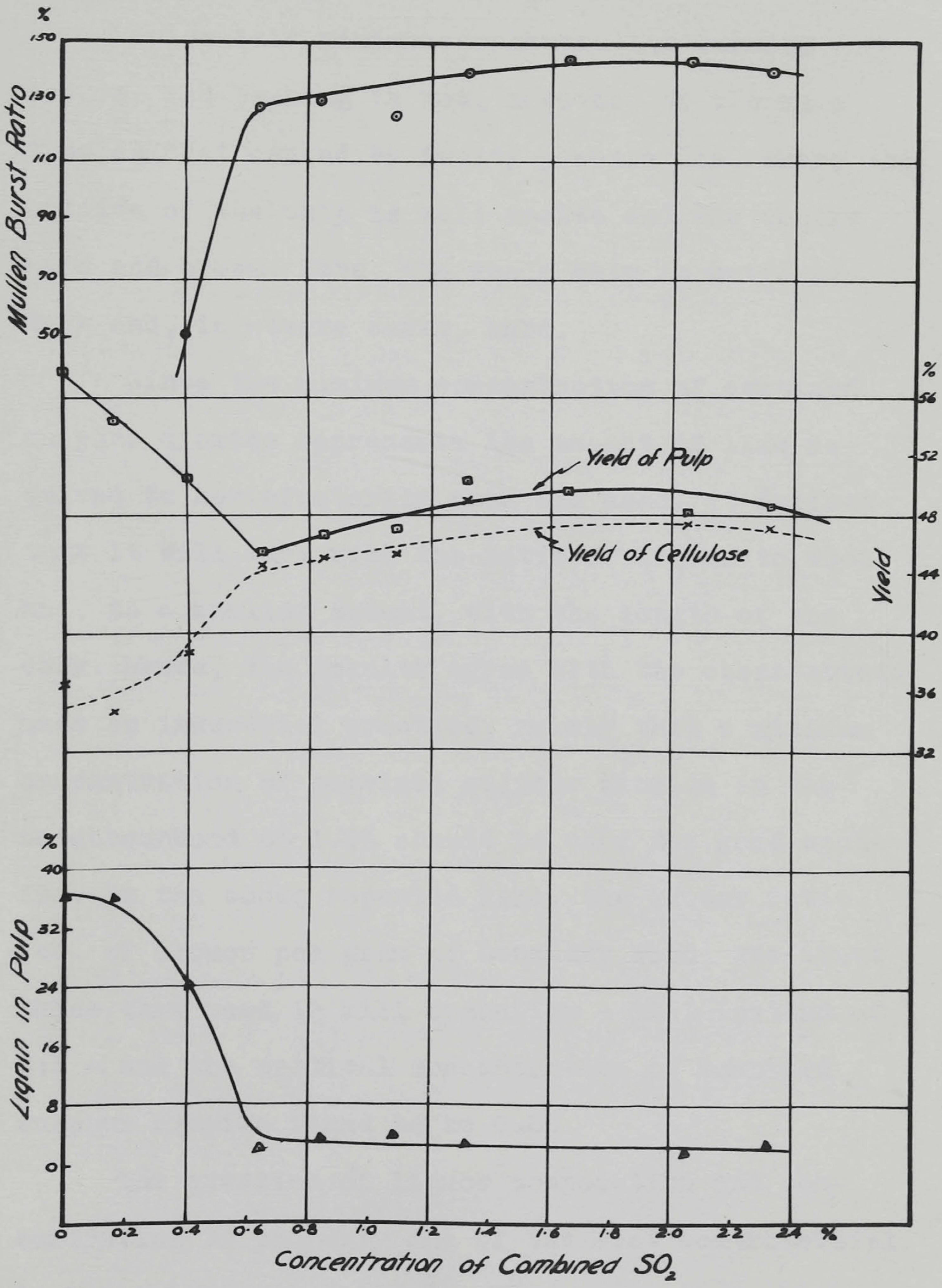
Runs #175 - 185 (Figure 16.)

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.34
Moisture - 9.0%
Cooking liquor - Free sulphur dioxide - 5.10%
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Combined SO_2 %	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
185	0.00	---	36.6	57.8	36.6	21.2
182	0.16	---	36.2	54.4	34.7	19.7
183	0.40	51	24.3	50.5	38.7	11.8
177	0.64	128	2.0	45.5	44.6	0.9
181	0.84	130	3.3	46.6	45.1	1.5
179	1.08	125	3.7	47.0	45.3	1.7
172	1.32	139	2.7	50.3	48.9	1.4
175	1.65	144	---	49.5	----	---
180	2.05	143	1.5	48.1	47.4	0.7
178	2.32	140	2.8	48.5	47.1	1.4

There is a very definite "critical" minimum concentration of combined sulphur dioxide necessary for satisfactory cooking. Above this minimum concentration, variations in pulp strength and yield are small; the variations in delignification are too small to be of any significance and are probably due

Figure 16.


%
150
130
110
90
70
50
Mullen Burst Ratio
%
56
52
48
44
40
36
32
Yield
Yield of Pulp
Yield of Cellulose
%
40
32
24
16
8
0
Lignin in Pulp
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
%
Concentration of Combined SO2

to small differences in the free sulphur dioxide concentration and in liquor ratio.

Below this minimum concentration burning occurs. The burning is not, however, of the same type as that caused by faulty penetration, where the outside of the chip is well cooked and the centre hard and brown. Here, the whole chip is uniformly dark and, in severe cases, hard.

Since the minimum concentration of combined sulphur dioxide represents the amount of lime required to satisfactorily cook the wood, it follows that it will vary with the ratio of liquor to wood and, to a smaller extent, with the length of the cook. Hence, the results agree with the observations made in industrial practice, namely that a minimum concentration of combined sulphur dioxide in the neighbourhood of 1.0% should be used for good cooking. In the cooks reported here, the liquor ratio (cc. of liquor per gram of bone-dry wood) was about twice that used in mill operation - 10:1 instead of 5:1 - and the critical concentration of combined sulphur dioxide found to be 0.5%

The question of liquor composition and concentration is probably one of the most controversial in the sulphite industry[44]. The reason is to be found in the wide variations in digester operation in different mills, when one considers that, once a sulphite cook is under way, the concentration of free sulphur dioxide in the liquor is almost wholly fixed by the temperature schedule used and by the method of handling relief, and this irrespective of the initial concentration of free sulphur dioxide. Consequently, the final result of a cook will be far more closely governed by digester operation than by liquor concentration. The general consensus of opinion, however, is that a high concentration of free sulphur dioxide is beneficial inasmuch as this free sulphur dioxide is kept in the digester, and that any concentration of combined sulphur dioxide in excess of the minimum required for satisfactory cooking is of little consequence.

Hägglund[45] reports that an increase in total sulphur dioxide from 4.3% to 8% increased the yield of defiberable material from 5 to 10% on the weight of the wood. He also states that an increase in lime content from 0.9% to 1.1% increased the pulp yield by about 3%.

Chidester and McGovern[46] report experiments carried out on a semi-commercial scale and at 75 lbs./sq.in. maximum pressure. They found that an increase in concentration up to 5.5% excess sulphur dioxide produced a small but definite increase in the rate of cooking. Any further increase in concentration caused only negligible increase in cooking speed.

Influence of dissolved carbon dioxide in the cooking liquor

These cooks were designed to fit in with the forced penetration experiments using saturated solutions of carbon dioxide. Cooking liquor of known combined sulphur dioxide concentration was put into the reservoir (15) and carbon dioxide bubbled through slowly until the desired pressure was built up. The liquor was then allowed to stand two hours for saturation to be reached, carbon dioxide gas being added from time to time to maintain the pressure. Finally, a sample of liquor was then withdrawn through a narrow copper tube leading below the surface of an excess of iodine solution to prevent loss of sulphur dioxide on evolution of carbon dioxide. The excess iodine was titrated with standard sodium thiosulphate solution and the total and free sulphur dioxide thus found.

Run #186

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.33
Moisture - 7.2%
Cooking liquor - Total sulphur dioxide - 5.27%
Free - 4.03
Combined - 1.24

The liquor was saturated with carbon dioxide at 9 atmospheres.

Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^{h}00'$
kept at 140°C. for $3^{h}00'$
The cell was evacuated 30' at 1 cm. of Hg.

Mullen Burst Ratio - 145.5%
Lignin in pulp - 7.2%
Yield of pulp - 52.7%
Yield of cellulose - 48.9%
Residual lignin - 3.8%

Run #187

Same as Run #186 except that the cooking liquor contained no carbon dioxide.

Mullen Burst Ratio - 155%
Lignin in pulp - 3.3%
Yield of pulp - 50.0%
Yield of cellulose - 48.4%
Residual lignin - 1.6%

The dissolved carbon dioxide in the liquor in Run #186, involving gas evolution within the chip on rise of temperature and hindrance to diffusion, resulted in distinctly slower delignification and slightly decreased strength. The yield of cellulose was not affected. Therefore, it appears that natural penetration is affected by a gaseous phase in the wood just as was forced penetration. However, the differences observed in cooking results were too small to warrant continuing investigation along this line, especially since the carbon dioxide concentration used was far above any that might be encountered in practice.

Influence of wood density and structure

Past results indicated a relation between density of the wood and cooking results, and, moreover, that the importance of wood structure as a controlling factor was far greater than was intimated by the few allusions made to it in the literature.

Therefore, a number of black spruce samples of varying density and structure were cooked under identical conditions to investigate any such relationship.

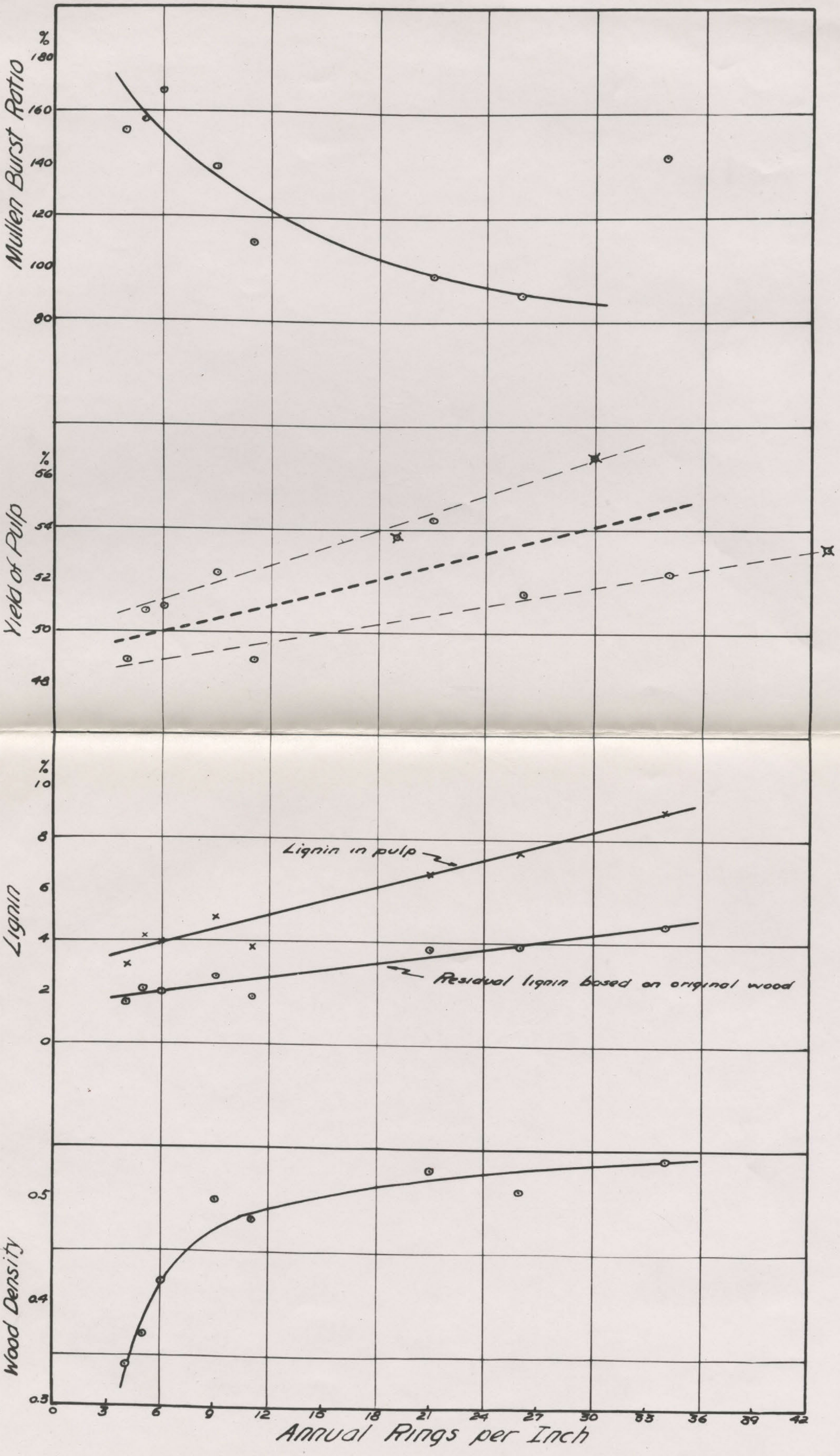
<u>Runs #195 - 200, 214 - 234</u> (Figure 17.)

Wood - Black Spruce heartwood
Chip length - 3/4"
Cooking liquor - Total sulphur dioxide - 5.20%
Free - 3.90
Combined - 1.30
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^{h}15'$
kept at 140°C. for $3^{h}00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run No.	Density	Rings per Inch	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
198 233	0.34	4	153	3.0	48.9	47.3	1.6
217 220	0.37	5	157	4.1	50.8	48.7	2.1
200	0.42	6	168	3.9	51.0	49.0	2.0
224 232	0.48	11	110	3.7	48.9	47.1	1.8
216	0.50	9	138.5	4.9	52.3	49.7	2.6
223	0.51	26	90	7.4	51.5	47.7	3.8
199	0.53	21	97.5	6.6	54.4	50.7	3.7
218 234	0.54	34	143	9.0	52.3	47.6	4.7

It is obvious that there can be no fundamental relationship between wood density and cooking results. There is a fairly definite trend towards decreasing delignification and increased pulp yield with increasing wood density, but there appears to be no relation between bursting strength of the pulp and the wood density. Plotting the data obtained on a

Figure 17.


Mullen Burst Ratio
%
180
160
140
120
100
80
Yield of Pulp
%
56
54
52
50
48
Lignin
%
10
8
6
4
2
0
Lignin in pulp
Residual lignin based on original wood
Wood Density
0.5
0.4
0.3
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
Annual Rings per Inch

basis of rings per inch gives a rather more satisfactory results. The delignification, expressed either as lignin in the pulp or as lignin calculated on the basis of the original wood, varies quite regularly with the annual rings per inch. There is a very definite trend towards lower bursting strength with increasing number of annual rings per inch in the wood. Yield variations are erratic, the trend being towards higher yield with increasing number of rings per inch. It is probably fortuitous that the yield values plotted on a base of rings per inch appear to fall on two widely separated lines.

The relation between density and annual rings is only an approximate one, the general relationship being that the slower growing wood has the higher density.

Three more samples were used, all three showing marked abnormalities. Two of the samples, of density 0.46 and 0.48, were of abnormally low density considering the large number of annual rings per inch. The third, of density 0.49, although showing a fairly normal number of annual rings, contained an abnormally high proportion of summer wood. The detailed results, obtained under the same conditions as those above, are given below -

Run No.	Density	Rings per Inch	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
215	0.46	30	111	5.2	56.8	53.8	3.0
195 213	0.48	43	73	5.0	53.2	50.6	2.6
214	0.49	19	58.5	5.3	53.7	51.0	2.7

The first two samples give points which lie far outside the curves obtained with the rest of the samples, except possibly the strength value of the 0.48 sample which appears fairly normal. The third sample gives fairly normal values for delignification and yield but the strength is abnormally low. This is no doubt due to the high proportion of what appeared to be summer wood, but which is more probably "rotholz", compression wood, since it occurred only on one side of the log. More will be said later of the relation of fibre characteristics to strength. The yield values for these three samples have been shown in Figure 17. by the symbol ¤

The above results do little beyond indicating the necessity for further work on a problem which is doubtless of great interest. It is obvious that density and rate of growth are not the only controlling factors of pulp quality. Future investigations should include more detailed study of the physical structure of the wood, such as determinations of proportion of summer and spring wood, fibre dimensions, rates of forced penetration, variations of wood structure in the same tree, etc.

In the small scale experiments, small samples of wood were used which could be considered quite homogeneous. High strength pulps were obtained. A shift to large scale experiments was invariably accompanied by a very definite decrease in pulp strength, in spite of practically identical cooking conditions. Variations in the homogeneity of the wood suggested itself as a potential explanation of the phenomenon, and a few experiments were made to investigate this in the small scale apparatus.

Run #192

Wood - Black Spruce
    Chip length - 3/4"
    3 chips - density 0.34
    3 chips - density 0.42
    3 chips - density 0.52

Cooking liquor -	Total sulphur dioxide	- 5.13%
	Free	- 3.82
	Combined	- 1.31

Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h15'$
    kept at 140°C. for $3^h15'$
The cell was evacuated 30' at 1 cm. of Hg.

Mullen Burst Ratio - 100%
Lignin in pulp - 4.6%
Yield of pulp - 50.2%
Yield of cellulose - 47.9%
Residual lignin on basis of wood - 2.3%

Run #194

Repetition of Run #192.

Mullen Burst Ratio - 117%
Lignin in pulp - 5.4%
Yield of pulp - 52.8%
Yield of cellulose - 50.0%
Residual lignin - 2.8%

These runs are not good checks, although close reproduction cannot be expected in this type of run, with such small amounts of wood. But one point is brought out quite clearly, namely that the cooking of woods of differing densities together produces a pulp whose bursting strength is far below the average strength of the pulps when the individual samples are cooked separately. Thus, in the case above, the average strength would be in the vicinity of 145%.

This was shown in another way. Samples of pulp from Runs #198 and #199 were mixed in equal proportion and a test hand-sheet made from the mixture. The sheet had a bursting strength of 114% whereas the average of the strengths of the pulps when tested separately was 125%. This was shown even more strikingly in connection with the runs reported below.

Run #214 indicated that the proportion of summer and spring wood in the wood might have an important effect on the strength of the resulting pulp. It was thought of interest to attempt cooking separately the spring and summer wood. However, spruce does not lend itself to separation of the two kinds of wood into samples of reasonable size. The experiments, therefore, were carried out on samples cut from a slice of Southern Pine, 14-1/2" in diameter and 32 years old. The heartwood was only 1-1/2" in diameter and was not used. The wood was thoroughly seasoned. The boundaries of the summer and spring wood were very sharp, making separation easy. The rings of summer wood were about 1/8" wide, and those of spring wood 1/4" wide or more. The density of the whole wood was 0.53, that of the springwood 0.29 and that of the summer wood 0.92, a surprisingly wide spread of density. The moisture content was 5.6% and the same for both spring and summer wood. The percentage of springwood in the whole wood, calculated on the basis of densities, was 62%.

Run #204

Wood - Southern Pine sapwood, Spring wood only
Chip length - 1/2"
Chip dimensions - 1/2" x 1/2" x 1/8"
Density - 0.29
Moisture - 5.6%
Cooking liquor - Total sulphur dioxide - 5.20%
Free - 3.83
Combined - 1.37
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^{h}00'$
kept at 140°C. for $3^{h}00'$
The cell was evacuated 30' at 1 cm. of Hg.

Run #204 (continued)

Mullen Burst Ratio - 148%
Lignin in pulp - 6.6%
Yield of pulp - 51.5%
Yield of cellulose - 48.1%
Residual lignin - 3.4%

Run #205

Wood - Southern Pine sapwood, Summer wood only.
Chip length - 1/2"
Chip dimensions - 1/2" x 1/2" x 1/8"
Density - 0.92
Moisture - 5.6%
Cooking liquor - Total sulphur dioxide - 5.20%
Free - 3.83
Combined - 1.37
Pressure - 10 atmospheres
Temperature - up to 100°C. in 30')
kept at 100°C. for $3^h30'$)
from 100 to 140°C. in 30')
kept at 140°C. for $4^h30'$) $9^h00'$
The cell was evacuated 30' at 1 cm. of Hg.
15 cc. liquor were withdrawn every hour beginning at the end of the fourth hour.

Mullen Burst Ratio - 25.6%
Lignin in pulp - 3.5%
Yield of pulp - 44.3%
Yield of cellulose - 42.7%
Residual lignin - 1.6%

In spite of the pre-evacuation, heating had to be very slow in Run#205 to avoid burning, because of the extraordinarily high density of the wood.

A sheet made of 40% pulp #205 and 60% pulp #204 gave a Mullen Burst Ratio of 52%, whereas if the strengths were simply additive, a Mullen Burst Ratio of 99% would result.

Run #206

Wood - Southern Pine sapwood
Both spring and summer wood, as naturally occurring, no separation made. 62% spring wood.
Chip length - 1/2"
Chip dimensions - 1/2" x 1" x 1/8"
Density - 0.53
Moisture - 5.6%

Otherwise same as Run #205.

Mullen Burst Ratio - 51.5%
Lignin in pulp - 4.75%
Yield of pulp - 46.1%
Yield of cellulose - 43.9%
Residual lignin - 2.2%

The results above require little comment. Microscopic examination of the fibers revealed differences in structure as marked as the discrepancies in strength. The spring wood fibres closely resembled spruce sulphite fibres in that they were wide, transparent, thin walled and flexible. The summer wood fibres, on the other hand, were narrow, thick walled, yellowish and stiff. The bordered pits were very evident on the spring wood fibres, but very few were discernible on the summer wood fibres.

It is interesting to note that the strength of the sheet made from the spring and summer wood pulps cooked separately was practically the same as that made from the whole wood pulp.

Little work of this nature is to be found in the literature, and the differences reported are usually quite small. As has been pointed out, this is to be expected from large scale work.

Jakimanskij[47] carried out penetration experiments and found that the rate of penetration of sulphite liquor into chips is dependent upon the wood density, that is, that the wider the annual rings, the more rapid was the penetration.

Lampen[48] cooked wood from logs where the width of the annual rings was 4.5, 1.5, and 0.45 mm. The fibre length of the fastest growing wood was 2.4 mm. and the breaking length of the pulp was 6765 metres. The other two samples had fibre lengths of 3 mm. and gave pulps of breaking lengths of 7595 and 7405 metres respectively. It is not known whether these figures apply to beaten or to unbeaten pulps.

Hägglund[49] cooked spring wood and summer wood separately and then refined the pulps to the same freeness. The breaking length was slightly greater for the pulp from the summer wood, but its resistance to folding considerably less.

The same investigator[34] also cooked chips from different parts of the same tree. The pulp made from the upper part of the tree was found to have lower strength than that from the middle part of the trunk. Pulp made from the branches was much weaker than either.

Influence of waste liquor and its relation to large scale cooking

There is another angle to the question of cooking different densities of wood simultaneously, as is involved in large scale work. That is the possible effect of the products of reaction on the course of the cooking process. The data in the literature on the effect of adding waste liquor to the cooking liquor is controversial and indefinite.

Monsson and Chidester[50] carried out cooks using up to 50% relief liquor and found no detectable change in the yield, colour, strength characteristics or chemical properties of the pulps obtained.

Chidester, Hrubesky and McGovern[51] found that the use of 50% and more relief liquor caused no apparent effect on the resulting pulps. They report that the use of waste liquor, up to nearly 100% caused a reduction in cooking time but a darkening in the colour of the pulp.

The Russian investigators, Fotjew, Eliaschberg and Martynow[52] claim slight disadvantages in the use of relief liquor, notably slightly poorer colour, although unchanged bleachability. The most noteworthy difference found was a 20-25% decrease in pulp strength. It is pointed out, however, that Scandinavian mills operating with waste liquor additions experienced no such decrease in strength.

Richter[35], reporting results of mill operation, draws cautious conclusions concerning the re-use of relief liquor. A slight decrease in strength was noted, but this was not very definite, and, furthermore conflicts with small scale experiments.

In the present investigation, it was observed when cooking mixed density wood in the two-litre bombs that the high density chips were not cooked as well as was expected from the small scale cooks. It was conceivable that the products of reaction might slow up the cooking reaction; in that case, the low density wood cooking faster than the high density wood, the concentration of organic matter in the liquor would build up faster than when the high density wood was cooked alone and the delignification might thus be decreased. The following experiments were planned to investigate this point.

Waste liquor from three small scale cooks was concentrated by distillation in vacuo from a volume of about 225 cc. to 15 cc. The concentrate was diluted to 150 cc. after filtration, again concentrated in vacuo to 15 cc. and diluted to 150 cc. This was mixed in the proportion of 70 cc. of waste liquor to 100 cc. of fresh liquor to bring the sulphur dioxide concentrations to the desired values.

Run #230

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.37
Moisture - 6.6%
Cooking liquor - Total sulphur dioxide - 5.30%
Free - 3.90
Combined - 1.40
41% waste liquor
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h00'$
kept at 140°C. for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Mullen Burst Ratio - 127%
Lignin in pulp - 6.3%
Yield of pulp - 49.1%
Yield of cellulose - 46.0%
Residual lignin - 3.1%

Runs #217 and 220

Same as Run #230 except that the cooking liquor contained no waste liquor.

Mullen Burst Ratio - 157%
Lignin in pulp - 4.1%
Yield of cellulose - 48.7%
Yield of pulp - 50.8%
Residual lignin - 2.1%

In the following run, wood of two densities was used, in equal proportions by volume. At the conclusion of the cook, the chips could easily be distinguished, since they retained their original shape, being only softened. The pulps from the two woods were treated separately by the usual procedure. The yield and lignin content were determined. Since the amounts of pulp were very small, strength tests were not made.

Run # 231

Wood - Black Spruce heartwood
Chip length - 3/4"
4 chips - density 0.51 moisture - 9.2%
4 chips - density 0.34 moisture - 6.6%
Cooking liquor - Total sulphur dioxide - 5.15%
Free - 3.90
Combined - 1.25
Pressure - 10 atmospheres
Temperature - up to 140°C. in $1^h15'$
kept at 140°C for $3^h00'$
The cell was evacuated 30' at 1 cm. of Hg.

Wood, density - 0.51

	Run #231	Cooked alone
Lignin in pulp -	9.1%	7.4%
Yield of pulp -	50.4	51.5
Yield of cellulose -	45.8	47.7
Residual lignin -	4.6	3.8

Wood, density - 0.34

Lignin in pulp -	3.4%	3.0%
Yield of pulp -	50.5	48.9
Yield of cellulose -	48.8	47.3
Residual lignin -	1.7	1.6

These experiments indicate that the addition of waste liquor does decrease delignification and also the yield both of pulp and of cellulose. There is also a marked decrease in the bursting strength. In the cook where two densities of wood were used, there was little change in the results obtained on the lower density wood, if anything there was a rise in the yields of pulp and cellulose. But there was a decrease in yield of both pulp and cellulose and decreased delignification in the case of the higher density wood.

This effect involves a further complication in the cooking of wood on a large scale. Large scale cooking entails using wood of often widely differing densities. This means that to obtain low screenings, the cooking must be carried on long enough to produce sufficient delignification of the high density wood. This results in overcooking of the low density wood, causing a further lowering in pulp strength superimposed on that inherent in the mixing of pulps originating from woods of differing density. It is realised that, on a mill operation scale, this is a practically insuperable difficulty. Yet, grading of pulpwood on a basis of density has often been recommended, and, in the light of the above experiments appears highly desirable.

The effect of waste liquor in decreasing delignification and cellulose yield must be traced to the increased acidity of the liquor, since lignin sulphonic acid has been shown to be an acid almost comparable in strength to the mineral acids. This point has already been discussed in a previous section and need not be amplified here.

In the case of mixed density cooks, another effect may come into play. The low density wood cooking faster, the high density wood will be cooked in liquor having a lower average effective sulphur dioxide concentration. This is probably at least partly responsible for the decreased delignification of the high density wood as compared to cooking the same wood alone, although it cannot be made to explain lowered pulp strength.

MISCELLANEOUS EXPERIMENTS

Influence of resins on rate of forced penetration through jack pine

The difficulty of cooking jack pine by the sulphite process has been often attributed to the high resin content. It was thought of interest to determine whether the removal of resins by ether extraction would have any effect on the rate of penetration.

A 3/4" chip of unseasoned jack pine (Run #27) was soaked in water 18 hours, after pre-evacuation, and the rate of forced penetration of water through it measured under a pressure differential of 6 atmospheres. Ether was then forced through the chip for 5-1/2 hours, also under a pressure differential of 6 atmospheres. The rate of penetration of the ether, of the order of 0.1 cc. per minute, was unexpectedly low, considering the low viscosity of the solvent. At the end of the ether extraction, water penetration was resumed under the original conditions until the equilibrium rate was reached, this requiring 1-1/2 hours.

Rate of penetration before extraction - 0.128 cc./min.
Rate of penetration after extraction - 0.154 cc./min.

The rate of penetration showed an increase of 20% even though the ether extraction was not complete. It can be concluded, therefore, that the resins of jack pine are a hindrance to penetration. This is probably to be explained by the sealing of tori against the cell wall, or by the plugging of the perforations in the bordered pit membranes.

Sutherland[5] observed that heating a soaked sample of spruce wood to a temperature above 70°C. produced a permanent, irreversible increase in the rate of forced penetration of water through the sample. There was the possibility that this might not be the case with jack pine, due to softening and flow of the resins at higher temperatures in such a fashion as to further hinder penetration.

Consequently, the rate of forced penetration of water through a 3/4" chip of unseasoned jack pine was measured (Run #46) under a pressure differential of 6 atmospheres. When a steady rate of flow had been observed, flow was interrupted, the clamp heated to 95°C. and maintained at that temperature for one hour. At the end of this time, the cell was cooled and the rate of penetration was again measured.

Rate of penetration before heating - 0.118 cc./min.
Rate of penetration after heating - 0.277 cc./min.

The increase in rate of penetration caused by the heat treatment is appreciably larger than was observed by Sutherland on spruce. It shows at least that there is no tendency for the resins to flow so as to further hinder penetration, the indication being rather that any flow takes place in the opposite direction.

Influence of Wet Heat Pre-treatment of Wood on Cooking

The permanent increase in rate of penetration on heating the soaked chip to above 70°C. suggested a possible effect of this treatment on cooking results.

Two white spruce heartwood chips were cooked under the same conditions, one chip being untreated, the other having been soaked overnight after evacuation, then boiled for one hour in distilled water and then air-dried.

<u>Runs #39 and 41</u>

Wood - White Spruce heartwood
Chip length - 3/4"
Density - 0.39
Moisture - 13.3%
Cooking liquor - Total sulphur dioxide - 4.83%
Free - 3.47
Combined - 1.36
Pressure - 7 atmospheres
Temperature - up to 140°C. in $1^{h}00'$
kept at 140°C. for $2^{h}30'$
The cell was evacuated 30' at 1 cm. of Hg.

	Untreated	Heat-treated
Mullen Burst Ratio	162	136
Lignin in pulp	12.7	10.6
Yield of pulp	55.9	55.4
Yield of cellulose	48.9	49.5
Residual lignin	7.0	5.9

The effect observed was not very great except on the strength. Heat-treatment increased the delignification and lowered the bursting strength. This is in accord with easier penetration of the sulphur dioxide, although reduced cellulose might have been expected.

Influence of added reagents in cooking liquor

In view of results obtained by Larocque[53] of this laboratory in the course of an investigation on the soda cooking process, it appeared that pulp strengths might greatly be affected by neutral reagents added in small quantities to the cooking liquor, and which might act either as catalysts or as protective colloids. A few cooks were made to indicate any such possibilities in sulphite cooking.

Runs #187 - 191

Wood - Black Spruce heartwood
Chip length - 3/4"
Density - 0.33
Moisture - 7.2%
Cooking liquor - Total sulphur dioxide - 5.27%
Free - 4.03
Combined - 1.24
Pressure - 10 atmospheres
Temperature - up to 140°C. in 1ʰ00'
kept at 140°C. for 3ʰ00'
The cell was evacuated 30' at 1 cm, of Hg.

Run No.	Added Reagent (a)	Mullen Burst Ratio %	Lignin in Pulp %	Yield of Pulp %	Yield of Cell. %	Residual Lignin %
187	None	155	3.3	50.0	48.4	1.6
188	Glycerine	151.5	4.0	49.4	47.4	2.0
189	Triethanol amine	172.5	5.8	52.5	49.8	2.7
190	Gelatin	115	2.7	45.1	44.3	1.2
(b)191	Gelatin	139	---	52.0	----	---

(a) all reagents added in concentration of 2% of liquor by weight.
(b) cook kept at 140°C. for 2ʰ30'

These few results show that organic materials added in small quantities to the cooking liquor can have a very marked effect on the pulp strength and on the speed of delignification.

The possibilities of investigation along this line are, evidently, boundless. Since, however, this line of attack is outside the scope of the present research, it was not continued.

Reddening of sulphite pulps

The strengths of pulps prepared in the two-litre bombs were invariably lower than those prepared on a small scale. There was another immediately noticeable and striking difference. The pulps prepared from small scale cooks were disintegrated and washed with distilled water; their colour ranged from almost pure white to varying shades of yellow. Those made on the larger scale were treated with tap water and turned pink - the typical reddening of industrial sulphite pulp.

It was just conceivable that there might be some connection between the two observations, i.e. that some sorption or oxidation phenomenon on treatment with tap water might so affect the surface of the fibres as to lower their bonding power and hence the strength of the sheet made from them.

Consequently, a small scale cook (Run #51) was made, using black spruce of density 0.37, and the resulting cooked chips were divided into two lots. One lot was disintegrated and washed in distilled water; the pulp was very light in colour. The other lot was disintegrated in tap water and the pulp washed with a large volume of hot tap water. This pulp was a deep pink. The strength tests on both were identical, 140.5% for that washed in distilled water, 141% for that washed in tap water.

There was marked difference in the colour of the two dried sheets, but this difference slowly disappeared on long standing, until the two sheets became indistinguishable.

SUMMARY AND CONCLUSIONS

The conclusions to be drawn from the researches described are of two kinds, (a) experimental results or statements of facts, and (b) theories of supposed mechanisms. The former will be given first and in as concise a manner as possible in the summary below. From these, information of immediate practical importance can be drawn in regard to mill procedure. Irrespective of the latter, which must be regarded as tentative, the writer feels that considerable time is required for the interpretation and correlation of all the facts found, hence the use of the term tentative. Though the promulgation of theories in making investigations of this kind is stimulating, they may be of even greater practical value in the future than the unrelated but definite results of each of the separate items. As a guide to the direction which future experimental work is to take, they are of immediate importance.

Summary

1. The simultaneous penetration of two phases through wood is slower than that of a single phase.
2. A forced flow of cooking liquor through the wood

during cooking increases the rate of delignification.

3. A preliminary evacuation of wood makes possible a much more rapid rise in temperature when cooking without the occurrence of burning. The effect is not one of prevention of sulphuric acid formation, but one of accelerated penetration.
4. Any intermediate reaction preceding final solubilization of lignin is more rapid than the reaction which results in a burnt cook.
5. For low density wood, there is a critical evacuation pressure above which burning occurs on rapid heating. With high density wood, there is no sharply defined critical value.
6. Preliminary repeated applications of sulphur dioxide gas pressure to the wood, alternating with relief, accelerate penetration of cooking liquor, just as does pre-evacuation.
7. The shortened cooking procedure made possible by pre-evacuation or by sulphur dioxide gas pre-treatment of the wood produces pulps with high bursting strengths.
8. Application of high hydrostatic pressure to the cooking liquor throughout the cook gives results approaching those given by pre-evacuation.

9. For low density wood, pre-evacuated before cooking, there is a critical moisture content above which burning occurs. With high density wood, the moisture content is less important.
10. There is an optimum maximum cooking temperature which depends on whether economic considerations or pulp quality specifications are the deciding factor.
11. Exposed surface of the chips, for constant chip length, only slightly affects rate of delignification. Under good cooking conditions, increased exposed surface results in decreased pulp strength. Burning may be eliminated by increase in exposed surface, an increase in pulp strength following.
12. There is a definite optimum cooking time which will vary with the density of the wood being cooked, liquor composition and maximum temperature.
13. Increase in free sulphur dioxide concentration in the cooking liquor accelerates delignification providing a sufficiently high pressure is maintained during the cook to hold the gas in solution. Increase in combined sulphur dioxide concentration above that required for satisfactory cooking has little influence on cooking results.

14. Wood structure has an important bearing on cooking results. With increase in rate of growth, there is a definite trend towards lower pulp yield, greater delignification and higher pulp strength. Several other factors, however, are involved, making the relation of wood structure to cooking results a very complicated one.
15. Uniformity of density of the wood cooked is even more important than the wood structure, heterogeneity resulting in markedly lowered pulp strength.
16. Spring wood can be cooked much more rapidly than summer wood from the same tree, and produces a pulp with much higher bursting strength.
17. Addition of waste liquor to the cooking liquor decreases the rate of delignification, the yield of cellulose and the strength of pulp.

Conclusions

The above leads to a number of practical conclusions, some of which may be well known to the sulphite expert, but upon which, judging by the literature, there does not appear to be complete agreement. A few examples will be given. The structure of wood plays an important part in governing the optimum cooking conditions and distinct advantages would be derived if wood could be graded into groups according to rate of growth and these cooked separately. The addition of waste liquor is slightly detrimental as far as pulp quality is concerned. The presence of small amounts of acid in the cooking liquor has little effect on the cooking of wood. These and similar conclusions are obvious and can be drawn immediately.

The contribution of most practical value is the development of a new cooking procedure which, in principle, may be made the basis of a modified commercial process. The essential features are a pre-treatment of the wood either by evacuation, by sulphur dioxide gas applications, or by a combination of both; a rapid rise to maximum cooking temperature; free sulphur dioxide concentration in the cooking liquor as high as permissible by pressure limitations; and a minimum of relief. It would be premature to give exact specifications for such a modified process without further work on a scale comparable to the industrial, although it is possible to do so from the data accumulated. Work on scales up to one cubic foot has shown that the principles involved are sound. The modified procedure makes possible the cooking of wood in about half the time currently taken, and produces pulps whose unbeaten strengths are far higher than the strength of normal sulphite pulp, pulps of Mullen Burst Ratio of 250% having been obtained. While such optimum results cannot be expected on a plant scale, they give limits which one can attempt to approach, even if they cannot be reached.

Enough has been said to indicate the practical value of the experimental results. It is perhaps worth while, however, to draw attention to one other point. While innumerable investigations have been carried out on separate factors influencing the sulphite process, it is doubtful if any one investigator has included in the same research the study of as many factors as have been dealt with in the present work where uniformity of procedure has made possible a better correlation of facts. For the same reason, the theoretical conclusions that can be drawn are perhaps of greater significance.

The two main purposes involved in the sulphite process are, on the one hand, the removal of lignin from wood, and, on the other hand, the production of as large a quantity of cellulose as possible, the latter with a minimum of degradation. Therefore, it seems logical to draw the theoretical conclusions from these two points of view.

The writer is neither competent to discuss nor directly concerned with the mechanism of the organic reactions which result in lignin removal. Rather, it is the relative rates of these reactions and the physical aspect of the entrance of the substances involved into the sphere of reaction which are of immediate interest. In this light, the early stages of the process, and those abnormal conditions resulting in a "burnt cook" are of particular interest.

Two theories have been advanced to explain the phenomenon of "burning" at the beginning of the sulphite cook. The majority of workers recognize that it is caused by incomplete penetration before the critical temperature is passed, and evidence has been advanced in this thesis in support of this theory. Some investigators[56] claim that the sulphonation of lignin occurs in stages, and that, to avoid burning, time must be allowed for one or more intermediate reactions to come to completion before the critical temperature is reached. Apart from the experimental evidence advanced against this interpretation, a further objection may be raised in that the explanation makes no provision for the part played by the base of the liquor. It has been shown that the presence of base in the wood definitely eliminates all danger of burning irrespective of the rate of heating, although it is not readily evident how the base might influence the actual sulphonation of the lignin. The effect of the base is rather to be attributed to its action in controlling the hydrogen ion concentration of the cooking liquor, and preventing its increase to a value which would result in the polymerisation of the sulphonated lignin. It is true that wood can be pulped with sulphur dioxide alone in the absence of base, but the temperature must be kept below the critical, and the quality of the pulp is far inferior to that produced by usual methods.

The vital importance of penetration in the sulphite process has been stressed throughout the work. This great importance might appear a little surprising in view of the negligible role played by penetration in the soda and kraft processes. This striking difference hinges on the hydrogen ion concentration of the cooking liquors. Since sulphite liquor is an acidic solution, its natural penetration into wood takes place along the tracheids of the wood, i.e. along the fibre direction; penetration at right angles is small in comparison. On the contrary, the alkaline cooking liquors penetrate wood with comparable velocities in all three structural directions, diffusing not only along the tracheids but also through the cell walls[59]. This distinction increases in importance with rise in temperature. So that, for a completely impregnated chip, concentration equilibrium is reached more rapidly with alkali than with acid. Moreover, inert gas occluded in the wood is not as serious an impediment to alkali penetration as to acid penetration, since solute diffusion is possible around the bubbles. With sulphite liquor, however, each bubble of gas acts as a barrier to diffusion as well as to liquid flow. This difference is enhanced by the vapour pressure differences of the liquors. The vapour pressure of alkaline liquors is materially the same as that of water, hence application of pressure will reduce the volume of the gaseous phase to that of the inert gas alone, even at higher temperatures. On the other hand, sulphite liquors have a high vapour pressure, which increases rapidly with rise in temperature. Gas bubbles serve as a nucleus for sulphur dioxide evaporation, so that pressure causes a much smaller reduction in volume, this effect emphasizing the hindrance to penetration offered by gas in the wood.

A further difference comes into play in the much greater solvent power of alkaline liquors, in comparison to sulphite liquor, on resins and allied substances. This has been shown by microscopic examination of pulps made by Stovel[57]. It was observed that, in sulphite pulp fibres, the pit membrane tori were always easily discernible, whereas, in alkaline pulp fibres, they were almost invariably totally absent, having been removed, presumably, by solution.

The behaviour of the cellulose of the wood during the course of the sulphite process is of particular interest, since it is the major factor in determining the quality of the final product, sulphite pulp, and its suitability for paper-making.

The bonding power of fibres is a function of the extent of their external surface and of the nature of that surface. Lampen[58] has shown that the length of fibres is not altered by sulphite cooking. It appears that the extent of the external surface of the fibres is not altered by the cooking process; therefore, the contribution of this factor to pulp strength is, in all probability, an intrinsic property of the wood from which the pulp is made. Variations in pulp strength with cooking conditions, therefore, must be traced to variations in the nature of this external surface, i.e. to varying degrees of degradation of this surface.

A method for measuring the projection areas of pulps by light absorption has been developed in these laboratories by Munro[11]. It was shown by Vivian, Mason and Maass[12], using this method, that changes in the extent of surface of a pulp brought about by beating entailed corresponding changes in bursting strength, and that the relation between extent of surface and strength was very definite for any one pulp.

The method was applied to some of the pulps obtained in the present work. The results, however, are not believed to be of sufficient accuracy to warrant definite conclusions, and consequently have not been reported in detail. The indications were that, for pulps prepared from the same wood by varying procedures, there appeared to be no relation between extent of surface and bursting strength. Moreover, soda pulp prepared from the same wood exhibited no marked difference in extent of surface, although the bursting strength was much lower. With pulps prepared from different woods by identical procedures, however, there appeared to be some indication of a relationship between extent of surface and bursting strength. The wide discrepancies in the bursting strengths of pulps prepared from the spring and summer wood from the same tree indicates the relationship to the extent of surface as apparent under the microscope. In this connection, it is quite likely that the rigidity of the summer wood fibres is a contributing factor to the low pulp strength in reducing the number of contact points between fibres in the sheet.

The lowered pulp strength resulting from cooking woods of different densities simultaneously can be explained by postulating a decrease of strength with surface degradation; for satisfactory cooking of the high density wood, the low density wood must be markedly overcooked, involving degradation of the fibre surface and loss of bonding power.

Suggested direction of future work

The investigation just described is by no means complete. Several of the factors affecting the course of the sulphite process have been rather cursorily examined; not a few of these might be studied more amply to advantage. Also many of these factors exert a mutual influence on one another - thus, the critical evacuation pressure will vary with the moisture content of the wood, the optimum cooking time will vary with the liquor composition, the temperature, the wood structure, etc. - and the study of these factors in pairs represents a vast amount of work. One form of hindrance to penetration, inert gas in the wood, has been dealt with at some length. Another still remains - the precipitate of calcium monosulphite thrown down from sulphite liquor under certain conditions. A study of this factor would involve comparative cooks with magnesium bisulphite liquors, and the investigation might be extended to include the use of sodium bisulphite and ammonium bisulphite liquors. Also, the precipitation of calcium monosulphite takes place most frequently from highly supersaturated solutions; a study of possible means of stabilizing this supersaturation, and thus preventing precipitation should prove interesting. The effect of added neutral reagents to the cooking liquor, capable of acting as catalysts or protective colloids has been merely pointed out and offers a virtually boundless field for study.

Pressure variations and methods of relief have not been investigated and will necessitate slight modifications in the apparatus.

One of the most attractive lines along which this research might be continued is a detailed study of the effect of wood structure on the properties of the resulting sulphite pulp. Such an investigation could make important contributions to the allied problem concerning the relation of fibre characteristics to pulp strength and sheet formation. The method of measurement of projection areas of pulps, which is at present being perfected, should prove of valuable assistance.

APPENDIX

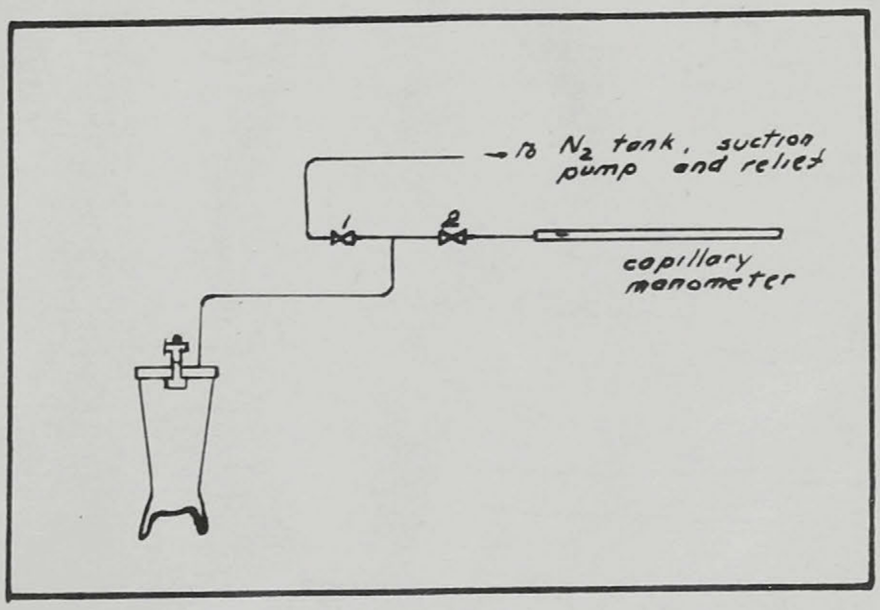
In this section are included a group of runs which clearly gave abnormal results and which do not fit in with the rest of the work. The abnormality was from the point of view of pulp strengths. This work was carried out during the latter part of July and all of August. During this time, it was impossible to test sheets under standard humidity conditions owing to break-down of the air-conditioning equipment. However, rough tests carried out in a small humidity chamber eliminated this explanation of the wide discrepancies observed.

The work is presented in the order in which it was carried out.

The low strengths first obtained coincided with a change in the apparatus. The usual set-up was not suited to the study of the effect of liquor ratio, due to the liquor contained in the connecting tubing, it being impossible to correct for back-diffusion of the reagents; nor was the set-up suited to the study of pressure effects owing to the impractibility of positive relief.

Consequently, it was decided to use one of the small bronze bombs used for experimental cooks by the Forest Products Laboratories of Canada. The bomb was slightly more than 5" high overall, and stood on four 1" legs. The inside diameter at the top was 2-1/4" and slightly less at the bottom. with a cover, grooved to receive a gasket, held in place by a simple yoke-type clamp. The capacity of the bomb was 220 cc. and could easily hold 25 g. of wood.

A length of 1/8" copper tubing was soldered into the cover and the bomb connected as in the diagram below.



The weighed chips were placed in the bomb and held in place by a thin perforated lead plate which prevented them from floating in the liquor. The bomb was assembled and connected in place. After evacuation through valve (1) - valve (2) being closed -

a measured amount of liquor was allowed to be sucked in. Pressure could be built up as desired by means of nitrogen. Valve (1) also served as a relief valve to control the pressure during the run. At the conclusion of the run, the bomb was quenched in a pail of cold water, the bomb opened and the chips treated in the usual fashion.

Run #102

Wood - Black Spruce heartwood
Chip length - 2.0 cm.
Chip dimensions - 2 x 2 x 1/2 cm.
Density - 0.41
Moisture - 8.4%
Cooking liquor - Total sulphur dioxide - 4.81%
Free - 3.51
Combined - 1.30
Pressure - 7 atmospheres throughout cook.
Liquor Ratio - 10 cc./gm. of wood
Temperature - up to 110°C. in 30')
kept at 110°C. for 30')
from 110 to 140°C. in 15')
kept at 140°C. for $3^{h}30'$) $4^{h}45'$
The cell was evacuated 30' at 1 cm. of Hg.

The chips were very soft, but very dirty. Those at the bottom of the bomb appeared to be slightly softer than those at the top.

Mullen Burst Ratio - 83.5%
Lignin in pulp - 4.6%
Yield of pulp - 52.7%
Yield of cellulose - 50.3%
Residual lignin - 2.4%

Run #103

Same as conditions in Run #102 except
Liquor ratio - 4 cc./gm. of wood.

Cooking was uneven. A few chips, near the surface of the liquor, appeared raw. Those in the centre of the bomb were soft and had been well cooked, while those at the bottom were very soft and had burned slightly at the end of the cook. A few chips on the top were removed, and the remainder divided into two portions.

	Centre portion	Bottom portion
Mullen Burst Ratio	76.5%	74.5%
Lignin in pulp	7.7%	5.5%
Yield of pulp overall	54.1%	

The uneven cooking was attributable to the large gas phase and to relief, the liquor near the surface losing a large part of its free sulphur dioxide and a concentration gradient being set up from the top to the bottom of the bomb. A connection between the final concentration of free sulphur dioxide in the waste liquor and pulp strength was indicated.

The following run was an attempt at reducing the change in liquor concentration, by having a small gas phase and a minimum of relief.

Run #104

Conditions same as in Run #102, except that a larger charge was used so as to almost fill the bomb. The pressure was raised at the beginning of the cook to 7 atmospheres by means of nitrogen, then allowed to rise on heating to 11 atmospheres and maintained at that value by relief.

The chips were very soft, but very dirty. Cooking appeared to be quite uniform.

Mullen Burst Ratio - 85.5%
Lignin in pulp - 1.85%
Yield of pulp - 46.0%
Yield of cellulose - 45.2%
Residual lignin - 0.8%

The increase in pressure resulted in much greater delignification; still, the low strength could scarcely be attributed to overcooking.

It was just conceivable that a catalytic effect might be involved, the catalyst being supplied by the material of the cell. Two possibilities presented themselves; either the Allegheny metal had a beneficial effect or the bronze had a detrimental effect. The first possibility appeared the more plausible in view of the fact that the strengths of the pulps obtained in the Allegheny metal cell were much above normal; the second seemed remote, considering the copper leads to the Allegheny metal cell, and the fact that the low pulp strengths just obtained were about of the order of magnitude of that of commercial sulphite pulp. Nevertheless, these possibilities were investigated. Since the point of predominating importance was the strength of the pulp, lignin determinations were not made in these and following runs, the pulp yield being taken as a sufficient index of delignification.

Run #105

Same conditions as in Run #104.

A hollow Allegheny metal cylinder, overall superficial area about 45 sq. cm., was placed in the bomb with the charge.

The chips were extremely soft.

Mullen Burst Ratio - 92%
Yield of pulp - 48.8%

The increase in strength was too small to be of any significance, other than that the Allegheny metal could have no marked effect, at least in a bronze bomb.

There remained the possibility of a detrimental effect of the bronze or copper. The Allegheny metal cell was reverted to, all outlets but one being sealed off, the remaining one being connected as in the case of the bronze bomb. The chips were surrounded by a cage of copper wire netting.

Run #106

Same conditions as in Runs #104 and #105, but carried out in the Allegheny metal cell, with chips enclosed in copper wire cage.

The chips were very soft but dirty.

Mullen Burst Ratio - 63.5%
Yield of pulp - 46.8%

The last two runs gave indications in favour of a detrimental effect of the copper. The next step was to cook in the Allegheny metal cell, but omitting the copper wire cage.

Run #107

Same donditions as in Run #106, but chips cooked loose without the copper wire cage.

Mullen Burst Ratio - 90%
Yield of pulp - 48.7%

The cooking liquor used in the last few runs was several days old and there were indications of oxidation.

Hence -

Run #108

Repetition of Run #107 using

Fresh cooking liquor - Total sulphur dioxide - 5.06%
Free - 3.71
Combined - 1.35

Mullen Burst Ratio - 80%
Yield of pulp - 50.3%

Runs #107 and #108 appeared to eliminate any catalytic action, but rather to connect low pulp strength with the small differences in cooking conditions, namely the presence of a gas phase and positive gas relief. This, obviously suggested an attempt to reproduce earlier results by returning to the original form of apparatus.

Run #109

Same conditions as in Run #108 but carried out with the original small scale set-up.

The chips were quite soft, but raw and very slightly burned in the centre.

Mullen Burst Ratio - 113.5%
Yield of pulp - 51.6%

The return to original conditions, even though the cook was not a good one, gave a very definite increase in strength, and the previous loss of strength seemed to be tied down to the differences in cooking conditions.

Then followed a series of five runs at varying cooking times. Inconsistent results were obtained, the bursting strengths fluctuating erratically between 90 and 110%.

During the course of the work, a layer of very hard, firmly adhering scale had formed on the walls of the cooking cell. A rough qualitative test performed on a small amount of this scale gave a distinct test for copper. Therefore, there remained the possibility of contamination of the system and of the hypothetical detrimental catalytic effect of copper. So the cell was completely dismantled, thoroughly cleaned and scoured, and reassembled. A cook made in the cleaned cell, under original conditions, produced a pulp having a bursting strength of 108%. The low strength persisted and there appeared to be no clue to the cause of the disappearance of the high strengths formerly obtained.

It would be superfluous to give the details of the twenty-one runs which followed in futile attempts to reproduce earlier results. Various samples of wood were used; the tank of sulphur dioxide used to prepare the cooking liquor having run low, a new tank was procured to eliminate the danger of the presence of more sulphur trioxide than could be absorbed by the washing train; cooks were made using magnesium instead of calcium as the base. Following the cleaning out of the cell, a pronounced tendency for the chips to burn at the end of the cook was observed, pointing to faulty penetration of the lime. To correct this, the combined sulphur dioxide concentration was increased, liquor flow through the cell during the cook was used, the chip length was halved, forced penetration cooks were made, all to no avail.

However, during these runs, there was a somewhat erratic but none the less unmistakably definite trend towards higher strengths, almost irrespective of cooking conditions. Finally, in Run #137, a new sample of wood was again tried and gave almost exactly the results which might have been predicted on the basis of the earlier work. Succeeding runs followed a normal course and the peculiar phenomena reported above never again repeated themselves.

The writer does not propose to offer any explanation for this disconcerting break in the course of the investigation. Any attempt to do so would be pure conjecture. To invoke a catalytic effect of copper followed by a gradual return to normal conditions accompanying a slow removal of the catalyst from the system appears tempting; however, the evidence is not sufficient to warrant such an hypothesis.

It is regretted that time was not available to observe the effect of a second introduction of copper into the cooking cell. The risk of another long series of poor results could not be incurred. It is hoped that the opportunity to investigate further these freak results will be available at some later date.

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