THE MECHANISM
OF THE
DELIGNIFICATION OF WOOD
IN
AQUEOUS SULPHITE SOLUTIONS

A STUDY OF THE MECHANISM OF THE DELIGNIFICATION OF WOOD IN AQUEOUS SULPHITE SOLUTIONS

A Thesis

Submitted to
The Faculty of Graduate Studies and Research
of McGill University
In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy.

by

John M. Calhoun

McGill University
April 1938.

ACKNOWLEDGMENTS

The writer wishes to express his sincere appreciation:

To Dr. O. Maass, for his valuable advice and constant encouragement throughout the course of this work.

To Dr. F. H. Yorston, for his many helpful suggestions and constructive criticism.

To A. J. Corey, for assistance in the experimental work described in Part I,A (1-5).

To J. J. R. Cannon, for assistance in the experimental work described in Part II,B.

To the National Research Council of Canada, for a Bursary (1936-37) and a Studentship (1937-38) which have made this work possible.

To the Forest Products Laboratories of Canada, Montreal, for the use of materials and equipment.

TABLE OF CONTENTS

EXPERIMENTAL

PART I

The Effect of Pretreating Wood in Aqueous Solutions on Subsequent Delignification in Sulphite Liquor

Results and Observations

A. Pretreatment in Buffer Solutions

B. Pretreatment in Neutral Salt Solutions

PART II

The Rate of Delignification of Untreated Spruce Wood in Sulphite Liquor

Results and Discussion

INTRODUCTION

The present investigation of the delignification of wood in aqueous sulphite solutions is, primarily, a study of the mechanism and kinetics of the chemical reactions which occur in the sulphite process, approached from the physico-chemical point of view. The specific factors studied were the effects of temperature, liquor composition and pretreatment of the wood sample on the rate of delignification. Although the theoretical significance of the experimental results will be emphasized throughout, the practical importance will be pointed out whenever possible.

That wood can be readily pulped by heating in bisulphite solutions, was discovered rather fortuitously about seventy years ago. Because of the rapid growth of the sulphite process to a major world industry, the commercial development far exceeded the theoretical. Consequently, it has only been in recent years that any systematic attempt has been made to determine the fundamental principles underlying each phase of the process. Although a great deal has already been accomplished, much more remains to be done and the present work was undertaken with the hope that it might assist in a clearer understanding of some of the reactions involved.

Because of the complexity of wood, its heterogeneity and the uncertainty regarding the chemical structure and properties of most of its constituents, this reaction is particularly difficult to study. The number of variables which may possibly influence the reaction are so large, that the experimental data must always be carefully analyzed before interpretation is possible. Many workers in this field in the past have attempted to study several variable factors at the same time and consequently many of their conclusions are open to question. In addition, there has been a regretable tendency to limit experimental conditions to the restricted range possible in commercial practise.

In the present work an attempt has been made to overcome these two objections. Experimental methods were chosen so that as many of the variable factors as possible could be held constant, and one isolated variable studied at a time. Frequently extreme conditions were used which are quite impossible on a commercial scale, but which give valuable information concerning the reactions involved, thus justifying their use.

Some of the variable factors which must be considered in any investigation of the sulphite process have been listed by de Montigny and Maass (19) somewhat as follows:

1. The wood species.
2. The wood density and structure.
3. The moisture content of the wood.
4. Pretreatment of the wood sample.
5. The size of the wood sample (size and shape of the chip, or particle size in the case of wood-meal).
6. The composition of the cooking liquor.

7. The liquor to wood ratio.
8. The rate of penetration of the cooking liquor.
9. The temperature.
10. The pressure.

Many of these factors have already been studied in this laboratory and are briefly reviewed in a later section. Those chosen to investigate more fully were Nos. 4, 6 and 9. Well seasoned, white spruce was used for the major part of the work. Only a few experiments were made with jack pine heart wood, merely to confirm the belief that certain phenomena observed were not peculiar to spruce. For the largest section of the work (Part II), the wood used was all taken from the same log. We can therefore eliminate the first two variable factors mentioned.

Only wood-meal or sawdust of 40 to 100 mesh, was used throughout this investigation. Such a procedure for laboratory experiments has received considerable criticism from workers in the industry who claim that results obtained by cooking sawdust, cannot be applied to commercial cooks with chips. This is partly true, but it is only by so simplifying the experimental conditions, that any fundamental investigation can be made. It is believed that the knowledge so gained will make possible a more intelligent study of the sulphite process under conditions approaching those used in commercial practise.

The most important advantage in using wood-meal for experimental cooks, is the elimination of penetration difficulties encountered with chips. It permits cooking at constant temperature, without danger of burning and thus immediately simplifies the temperature schedule. In addition, a more homogeneous material is obtained. The chief disadvantage in cooking wood-meal rather than chips is that no determinations of the strength of the pulps can be made, since it is impossible to form test sheets from the ground fibres. However, the advantages of using wood-meal far outweigh the disadvantages at this stage of the investigation.

The moisture content of the wood-meal (about 7%), which in the case of chips may affect the penetration of the liquor, was unimportant when cooking with wood-meal. The ratio of liquor to wood was held constant and was sufficiently high that dilution of the liquor by the moisture in the wood was negligible, and concentration changes during cooking due to consumption of lime and sulphur dioxide, were minimized.

All cooks made in the present work, were made at constant volume in small, sealed, bomb-type glass or metal digesters of 100 to 200 cc. capacity. No relief of gases during the cooking process was permitted, contrary to the custom in industrial practise. This prevented any loss of sulphur dioxide with consequent weakening of the cooking liquor. The pressure in any given cook was, therefore, dependent only on the composition and temperature of the liquor. In this manner, all the variable factors outlined above could be held constant, except the particular one chosen for study, which could be varied at will.

The experimental data has been presented chronologically and is divided into two, almost completely separate parts. The first deals with the effect of various types of pretreatment on subsequent delignification, and the second is concerned only with the effect of varying the liquor composition and the temperature, on the rate of delignification of untreated wood. There is a general section dealing with experimental methods common to the work as a whole, and in addition, specialized sections preceding each part.

Because of the nature of the work, some discussion is given along with the experimental data. However, each section is concluded by a summary and a more general discussion. An attempt has been made throughout to distinguish clearly between any speculation and the actual experimental facts on which it is based.

HISTORICAL AND THEORETICAL

Due to the increasing importance of the sulphite process for the manufacture of pulp, paper and other cellulose products, a vast amount of literature has been accumulated in recent years. Much of the information is difficult to correlate and interpret because of the many varied experimental conditions which were used, and frequently it is hard to distinguish between actual investigation and mere conjecture. Unless a thorough, critical discussion were given of the results of each worker, such a review would only confuse the issue, and this is impossible within the confines of one thesis. Therefore only information which bears directly on the present work will be mentioned.

A brief description of the development of the commercial sulphite process will first be given to assist in a clearer understanding of subsequent discussions. This will be followed by a short review of previous investigations carried out at McGill University, which led up to the present work. The chemistry of wood and its constituents, and current theories regarding the reactions between wood and sulphite solutions, will be briefly discussed. Those desiring a more detailed knowledge may be referred to standard text books on the subject (14, 37, 62, 67).

1. The Manufacture of Sulphite Pulp

The process for producing pulp by heating wood in aqueous solutions of sulphur dioxide together with calcium or magnesium bisulphite, was first patented in England in 1867 by B. C. Tilghman. Mechanical difficulties delayed commercial developments and it was not until 1874 that the first sulphite mill was constructed and operated by C. D. Ekman in Sweden. At the same time, A. Mitscherlich was developing a sulphite process in Germany which commenced production about 1880.

At the present time there are two different methods in common use; the direct or quick-cook process and the indirect or slow-cook, Mitscherlich process. Chips of wood about 3/4 inch long, are charged into steel digesters of 12 to 18 tons capacity, lined with acid resistant brick. Cooking liquor containing 0.8 to 1.2% combined and about 5.5% total sulphur dioxide is added.

In the quick-cook process most common in North America, steam is injected directly into the bottom of the digester and the temperature raised according to a definite schedule. Usually the digester is brought up to 110°C. in 3 or 4 hours, and gradually raised to 135° to 145°C. However, actual temperature schedules vary with the kind of wood, the strength of the acid, the quality of the pulp desired, previous experience in a particular mill, etc. A maximum pressure of 70 to 80 pounds is usually maintained by relieving some of the digester gases at suitable intervals. The sulphur dioxide is recovered and used again. Completion of the cook requires about 10 to 12 hours and is determined by analysis of samples of the liquor withdrawn from the digester. The blowoff valve is then opened and the charge forced into a blow-pit against a metal target, which helps disintegrate the pulp. Subsequent treatment, consisting of washing, screening, bleaching, etc., depends on the type of product desired.

In the slow-cook or Mitscherlich process, the steam is not introduced directly into the digester, but is passed through lead or copper coils placed at the bottom. Consequently, no dilution of the cooking liquor by the steam occurs. The maximum temperature reached is usually 120°C., and the maximum pressure 60 pounds. The duration of the cook may be from 30 to 40 hours. The advantages claimed for this process are higher yields of better quality pulp.

2. Sulphite Pulping and Related Studies Carried Out at McGill University

In 1927 a systematic investigation of problems related to sulphite pulping was commenced under the direction of Dr. O. Maass in the Department of Physical Chemistry, McGill University, in co-operation with the Forest Products Laboratories of Canada, Montreal. Two general lines of research were undertaken. The first involved a fundamental study of the pure components of sulphite liquor and their phase relationships. The second consisted of a study of various physico-chemical factors related to wood itself.

The fundamental investigations were commenced by C. Maass (49), who measured the vapor density of pure sulphur dioxide, and the vapor pressure and conductivity of its aqueous solutions below 27°C. W. B. Campbell (11) extended the study of equilibrium in sulphur dioxide solutions to 120°C. over a wide concentration range. Since 1930, Grieve (26), Gurd (27), Gishler (23, 24, 25), and Beazley (3,4) have investigated the three component system, calcium oxide - sulphur dioxide - water. The equilibrium data obtained, made possible the calculation of ion concentrations at various temperatures, and have proved invaluable in the study of sulphite pulping. Frequent use of them will be made throughout the present work.

Since the satisfactory penetration of sulphite liquor into the wood chip is one of the important problems in commercial pulping, a thorough investigation of this factor was the first step in a more direct attack. In 1927 Johnston (42) commenced a study of the forced penetration of liquids into jack pine. This was continued in 1930 by Sutherland (68) and the effects of wood species, thickness of section, direction of flow, temperature, pressure, etc., on the rate of penetration of water were determined.

Saunderson (59, 60) extended the investigation to include both natural and forced penetration of sulphite liquor into wood. He showed that the free sulphur dioxide diffuses more rapidly into wood than does the combined, and that the rate of forced penetration increases with the concentration of the free sulphur dioxide under the same pressure differential. This was an important contribution because of its relation to "burning", a phenomenon which occurs in sulphite pulping when too high a temperature is reached before the lime has penetrated into the chip.

Saunderson also showed that above 70°C., the rate of forced penetration of sulphite liquor through spruce wood, was permanently altered due to the cooking action. The rate of delignification was found to be more rapid when a continuous flow of sulphite liquor was forced through the wood, indicating the importance of satisfactory penetration in the pulping process. Pre-evacuation of chips increased the rate of natural penetration a thousand fold, showing that the presence of air inside the wood presented the greatest hindrance to penetration.

De Montigny (19) in 1933 continued the penetration studies and commenced an investigation of other physico-chemical factors which influence sulphite pulping. Applying Saunderson's observation that the presence of air within the chip, greatly hindered penetration, de Montigny developed a pre-evacuation technique by which chips could be heated in sulphite liquor much more rapidly, without danger of burning. A second method of removing the air from within the chip consisted of applying gaseous sulphur dioxide under pressure, alternated with relief, until the partial pressure of the air was reduced to a negligible quantity.

De Montigny made a few experiments on the effect of varying the liquor composition on the rate of delignification. Only a small range of concentration was covered, constant volume and constant concentration conditions were not preserved, and precipitation of calcium sulphite was not considered. His results are, therefore, only of a qualitative nature, but show that an increase in the concentration of free sulphur dioxide increases the rate of delignification, provided sufficient pressure is maintained to hold all of the gas in solution. An increase in the combined sulphur dioxide above a certain minimum (equal to about 5% of the weight of the wood), appeared to have no influence on the rate of cooking. The effect of wood density and structure; rate of growth of the tree; heartwood, sapwood, springwood and summerwood; size, shape and moisture content of the chips, etc., on cooking properties and quality of pulp was investigated.

Corey (15) in 1934 commenced an investigation of sulphite pulping, more directly related to a study of the reaction between lignin and bisulphite solutions. He measured the rate of delignification of spruce wood-meal and chips and found that the reaction was only approximately first order, and that systematic deviations from this relationship were apparent. The reaction obeyed the Arrhenius equation between 100° and 140°C. and the temperature coefficient was found to be approximately 2.0 per 10° interval over the range measured. A value of 21,000 cal. per gm. mol. was calculated for "E", the energy of activation, but no theoretical interpretations were attempted.

A number of curious phenomena connected with the pretreatment of wood, were brought to light by Corey. When wood was heated several hours in water at 130°C., it became much more difficult to delignify under normal sulphite cooking conditions, Heating in an atmosphere of nitrogen or in toluene, had no apparent effect on subsequent cooking properties. Corey found that the above phenomenon was related to the hydrogen ion concentration of the aqueous solution in which the wood was pretreated, and that the effect was a minimum about pH 5. The hypothesis was advanced that the lignin was coagulated or polymerized in some manner which rendered subsequent cooking more difficult. That the effect was of a physical, rather than a purely chemical, nature was favoured. Since these results of Corey formed the starting point for the present work, they will be discussed more fully at a later stage.

3. The Chemistry of Wood and its Constituents

Due to the fact that wood is a biological product, its structure, both physically and chemically, is of a very complex nature. The chief constituents of wood are cellulose, lignin, carbohydrates, fats and resins, proteins, tannin and mineral matter. The chemical analysis of wood varies with different species and different locations. It may vary in different parts of the same tree and in springwood as compared with summerwood. Different results may be obtained by different methods of analysis for reasons which will be made clear below.

A typical analysis of some Canadian woods is given by Johnsen and Hovey (14, p.42) as follows:

	White spruce	Jack pine
Cellulose	56.48	49.24
Lignin	27.60	30.45
Fats and resins	0.99	1.61
Ash	0.25	0.18
Carbohydrates, etc. (by difference)	14.68	18.52

The distinction between cellulose and the lower carbohydrates present in wood is an arbitrary one, and explains why different analytical values are obtained by different workers, even on the same wood. Ordinary preparations of cellulose are not uniform materials, but mixtures. The cellulose fraction which is very resistant to ordinary chemical reagents is called alpha-cellulose, and represents about 40% of the wood. It is this material which is most important to the papermaker. Beta-cellulose and gamma-cellulose are fractions soluble in strong alkali, the former being reprecipitated on acidification. This classification is based on convenient methods of separation and does not imply three distinct chemical compounds.

Heuser (39) has presented evidence which indicates that purified alpha-cellulose from either wood, cotton or other sources is chemically identical. Its empirical formula is $(C_6H_{10}O_5)_n$ and it consists of a chain of anhydroglucose units of uncertain length. X-ray evidence indicates that these chains are arranged in a definite manner, forming tiny crystallites. Estimations of molecular weight vary from 4,000 to

200,000 and whether or not the original cellulose has a fixed molecular weight, any actual preparation contains chains of different length. In addition to celluloses there are lower polysaccharides present in wood, sometimes called "hemicelluloses", which consist chiefly of hexosans and pentosans. Hemicelluloses are more readily hydrolysed during the cooking process to simple sugars, which are found in the waste liquor.

The chemistry of lignin is more pertinent than that of cellulose to the present discussion, since it is the reaction between sulphite solutions and lignin, resulting in the removal of the latter from wood, with which we are mostly concerned. Unfortunately, even less is known about lignin than cellulose, although a large number of papers on the subject have been published. Only a brief outline of the more important observations can be given here, and the reader is referred to a recent thorough review with 300 references by Phillips (56) for further information.

Lignin is the cementing material present in wood which binds the cellulose fibres together and gives strength and rigidity to the cell wall. Whether lignin is chemically bound to cellulose or not, is still a matter of controversy. Most investigators now favour the opinion that lignin only forms a mechanical encrustation around the cellulose fibres, but others claim ester or ether linkages with cellulose. Lignin preparations have been isolated from wood in a variety of ways, but there is as yet, no known method by which it can be isolated unchanged. There is also some evidence that lignin as present in wood is not a homogeneous material. It is these facts which so complicate the study of lignin.

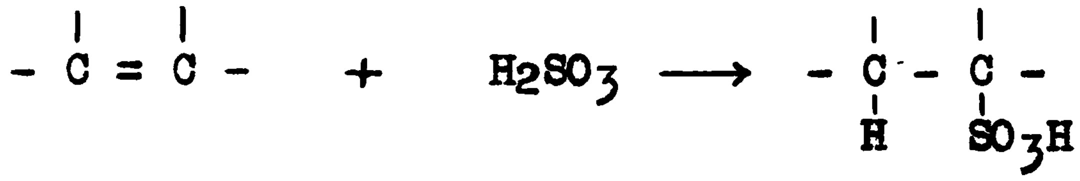
With regard to the structure of lignin, little can be said. Numerous formulae have been proposed on rather meagre evidence, and none can be considered more than speculative. There is considerable evidence to indicate that lignin contains either an aromatic or hydroaromatic nucleus, although some investigators maintain that it belongs to the aliphatic or heterocyclic series. The presence of methoxyl groups in lignin has been definitely established and Freudenberg (20) claims that they are attached to an aromatic nucleus. The presence of both alcoholic and phenolic hydroxyl groups has been claimed, but whether or not lignin contains free carbonyl groups is still unsettled. The presence of an ethylenic bond in lignin has not been definitely established according to Phillips (56), although Klason's hypothesis (43) for the reaction between sulphurous acid and lignin is based on such an assumption.

When lignified materials such as wood, are heated in a solution of calcium bisulphite containing an excess of sulphurous acid, the lignin is dissolved out leaving the cellulose in a more or less pure state. Lindsey and Tollens (48) first showed that lignin in waste sulphite liquor is present in the form of a calcium salt of a sulphonic acid. From a fractionation of the barium salts, it was concluded that lignin sulphonic acids were mixtures and not uniform substances. Tomlinson and Hibbert (70) claim that the difference is not chemical but due only to a difference in the degree of molecular association. Hoover, Hunten and Sankey (41) and Hägglund and Johannson (32) have shown that lignin sulphonic acids are highly ionized and have an acidity comparable to that of strong mineral acids.

4. The Mechanism and Kinetics of the Reaction between Lignin and Bisulphite Solutions

Since our present day knowledge of the chemistry of lignin is so limited, the actual mechanism of the reaction between lignin and acid sulphites has been largely a matter of conjecture. A great many theories have been proposed in the literature, some of which are based on insufficient or contradictory evidence. Therefore, only the most important contributions will be mentioned.

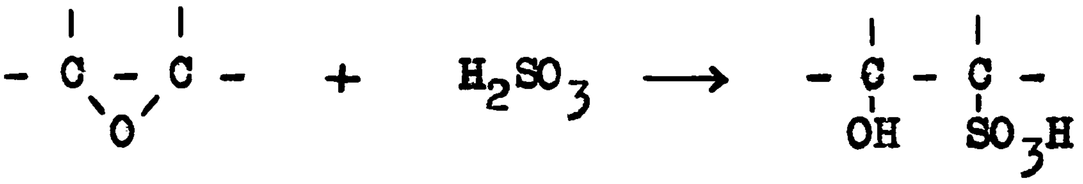
The group in the lignin molecule to which the sulphurous acid adds is still a matter of debate. According to Klason (43), addition takes place at an ethylenic bond:



$$-\overset{|}{C}=\overset{|}{C}- \quad + \quad H_2SO_3 \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{SO_3H}{\overset{|}{\underset{|}{C}}}-$$

He claims that lignin combines with four molecules of sulphurous acid, only two of which form sulphonic acid groups. To account for the more loosely combined sulphurous acid, Klason postulates an aldehyde carbonyl bond conjugate to the ethylene bond.

The presence of a true ethylene bond in natural lignin appears to be extremely doubtful. To overcome this objection, it has been suggested that the ethylene bond is formed during the reaction by the elimination of a molecule of water from adjacent carbon atoms. Hägglund (31) favours a methylene oxide or larger oxide ring, which ruptures with the addition of sulphurous acid:



More recently Freudenberg (21) has come out in favour of direct substitution of a sulphonic acid group in a benzene ring, while Tomlinson and Hibbert (70) found evidence of a sulphonic acid group adjacent to the vanillin nucleus. However, a discussion of these various hypotheses is not appropriate here, and the reader is referred elsewhere for more detailed information (56, 69).

The mechanism by which the sulphonated lignin is removed from the wood is even more obscure. Hägglund (28, 33) first proposed the theory that the delignification of wood took place in two distinct stages:

1. Sulphonation of the lignin in the solid phase to form a solid lignin - sulphonic - carbohydrate compound.

2. Hydrolysis of the lignin - sulphonic - carbohydrate compound in the solid phase, liberating a lignin sulphonate which is soluble.

Hägglund assumes a chemical attachment between lignin and carbohydrates, and claims that the sulphonation reaction is rapid compared with the hydrolysis reaction, and that the latter therefore determines the overall rate of delignification. The rate of sulphonation is determined by the bisulphite ion concentration and the rate of hydrolysis (and therefore the rate of delignification) by the hydrogen ion concentration.

In support of this theory Hägglund (29, 30) claims that if wood is cooked in a sodium bisulphite solution containing no excess sulphur dioxide (and therefore of low hydrogen ion concentration), the sulphonation proceeds normally, but the lignin is cooked out only very slowly. At the same time this sulphonated lignin is insoluble in water, but can be readily cooked out in buffer solutions at a rate proportional to the hydrogen ion concentration of the buffer. This last statement has been substantiated by Yorston (78), who showed that the rate of delignification in the buffer solution depended on the initial sulphur content of the lignin as well as on the pH of the buffer.

Hägglund's theory has received considerable support, although it has a number of weaknesses. That some kind of a sulphonation reaction takes place, cannot be doubted, but the reaction by which the sulphonated lignin is dissolved out is very uncertain. The assumption of a chemical bonding between lignin and carbohydrates is not justified by the experimental evidence. Yet, if such a union does not exist, what is being hydrolysed? Yorston (73, 74) has shown that the rate of sulphonation is slow enough to influence to some extent the overall rate of delignification. In the present work it will be shown that Hägglund's emphasis of the hydrogen ion concentration as the determining factor in the delignification of wood by the sulphite process is unjustified.

Michel-Jaffard (51) and Hägglund (33) mention without favour an alternative hypothesis as a possible explanation for the removal of sulphonated lignin from the wood, viz., that a depolymerization of the lignin may occur. It is significant that lignin isolated from wood by any known method, does not exhibit the same properties as natural lignin, particularly in regard to its behaviour toward acid sulphite solutions. Corey and Maass (16, 18) have shown that some of the phenomena, observed when wood is pretreated in acid solutions, can be explained on the basis of a coagulation of the lignin, and support the view that subsequent cooking may be a depolymerization process. In view of the colloidal nature of lignin, it is believed that this point of view has not received sufficient attention.

With regard to the kinetics of the delignification of wood in acid sulphite solutions, it is clear that the rate of reaction will depend on three factors, viz., the rate of penetration of the reagents into the wood fibre (including both penetration of the liquor and diffusion of the solute within the liquor), the rate of sulphonation of the lignin, and the rate of removal of the sulphonated lignin. By cooking finely divided wood-meal and using a sufficiently high liquor ratio, the first factor can be eliminated and the second and third studied.

It has been observed by a number of investigators that the cooking of wood by the sulphite process, approximates closely to a first order reaction., with respect to the lignin. That is, the overall rate of removal of lignin appears to be very nearly proportional to the quantity of lignin present at any instant. Expressed mathematically,

$$-\frac{dL}{dt} = k\,L \qquad \text{..................} \qquad (1)$$

On integration this becomes:

$$k = \frac{2.303}{t}\log\frac{Lo}{L} \qquad \text{..................} \qquad (2)$$

where k = the first order velocity constant,

L_o = the initial lignin content, and

L = the lignin content at time "t", both expressed as percent of the original wood.

When "log L" is plotted against "t" a straight line is obtained if the reaction is first order. This method of representation is particularly convenient and has been followed throughout the present work. It is deviations from this straight line, first order relationship which are of interest in a study of the kinetics of the reaction.

Stangeland (66) has made a considerable study of the kinetics of the sulphite process and his conclusions have been accepted by St. Klein (58). From a series of small scale cooks with wood-meal in sealed glass tubes, Stangeland determined the rate of removal of the "incrustants", or all substances other than Cross and Bevan cellulose. He claimed that the removal of incrustants was approximately first order and that this was evidence in support of Hägglund's theory of the mechanism of the reaction. If the rate of sulphonation of the lignin were rapid compared with the rate of hydrolysis of sulphonated lignin, the latter would determine the rate of delignification, and could conceivably be monomolecular. The hydrogen ion concentration of the liquor would therefore determine the rate of cooking at constant temperature.

Stangeland also claimed that since the incrustants other than lignin appeared to go into solution at the same rate as the latter, these substances must be chemically bound to the lignin molecule. The temperature coefficient for the removal of incrustants was found to be close to 2.0 per 10° interval between 110° and 140°C., from which Stangeland concluded that the rate of reaction was not determined by a diffusion process for which the temperature coefficient is known to be about 1.2 per 10°C.

Yorston (73) has made a critical study of Stangeland's results and pointed out that the calculation of velocity constants was based at each interval on the incrustant content of the original wood and not on the incrustant content at the previous period. This method of calculation tends to obscure any variation from the first order relationship, but in spite of this Stangeland's velocity constants do show considerable variation. Even if the lignin and other incrustants are dissolved separately according to the monomolecular law, the velocity constant for one reaction would have to be nearly twice that for the other, before the reaction considered as a whole would depart greatly from the first order relationship. Consequently Stangeland is not justified in assuming the existence of a chemically bound lignin-carbohydrate complex on the basis of his results. Miller and Swanson (52, p.89) have also presented considerable evidence to show that the removal of lignin and carbohydrates from wood is entirely independent of each other and due to the dual nature of sulphite liquor as a hydrolysis medium and a cooking agent. In addition there are a number of other equally plausible explanations to account for the removal of lignin, which do not require an hydrolysis reaction slow enough to determine the rate of delignification and controlled by the hydrogen ion concentration of the liquor.

Yorston (73) cooked spruce wood-meal at 130°C. in calcium base sulphite liquor and determined the rate of lignin removal. He showed that there was a systematic deviation from the first order relationship in that the rate of delignification increased during the first quarter of the cook, and the straight line portion of the curve, when plotted according to Equation (2), extrapolates to zero time at a lignin value considerably greater than that of the original wood. This has been substantiated by Corey and Maass (18).

Yorston offers three possible explanations to account for this:

(a) That all the lignin is not accessible to the cooking liquor and the rate is therefore proportional to the exposed surface of the lignin, which increases as the cooking proceeds.

(b) That the hydrogen ion concentration of the liquor increases sufficiently during the cooking, due to the formation of strong lignin sulphonic acids, to speed up the reaction. This appears doubtful because of the high liquor ratio used (37.5 : 1).

(c) That the delignification of wood in bisulphite solutions might be due to two consecutive first order reactions, the first of which is only approximately double the rate of the second. A mathematical analysis showed that under these conditions, the overall rate of reaction would deviate from the first order relationship in a manner similar to that found by experiment. Only when one reaction is considerably more rapid than the other, is the overall rate determined by the slowest reaction. This assumption in the present case by Hägglund and Stangeland, is not justified by experiment.

Yorston (74) developed this latter hypothesis, suggesting that the rate of sulphonation might be proportional to the amount of unsulphonated lignin present at any instant, and the rate of the second reaction might be proportional to the amount of sulphonated lignin present at any instant. An attempt to verify this was made by determining both the sulphur and the lignin content of the pulps at different stages in the cooking process. Mathematical expressions were derived based on the above assumptions, to show the variation in the amount of sulphonated and unsulphonated lignin with the time of cooking.

The theoretical curve for the rate of removal of lignin derived in the above manner was found to have the same slope as the experimental curve, but was displaced uniformly upward. That is, the actual lignin content of the pulps was less than predicted by the theory. This difference could be explained either by assuming that part of the lignin was more resistant than the remainder, or that the lignin was sulphonated beyond the amount required to bring it into solution. Up to the present time Yorston's theory has not received any more confirmation, but he has shown definitely that the sulphonation reaction is slow enough to limit to some extent the overall rate of delignification.

Corey and Maass (16), approaching the subject from an entirely different point of view, have suggested that the apparent unimolecularity of the reaction may be merely a coincidence due to the cancellation of two opposing tendencies. The effect of pretreating wood in aqueous solutions at cooking temperatures in retarding subsequent delignification, led to the conception of a polymerization or coagulation of the lignin. It was suggested that the cooking action of sulphite liquor might cause a depolymerization of the lignin, increasing the exposed surface and hence, the reaction rate. In a normal sulphite cook these two opposing tendencies might cancel each other, producing an approximate straight line relationship when the results are plotted according to Equation (2). However the writer believes that such a fortuitous coincidence is not very probable, and that it does not explain all the observed facts.

It is apparent that a great variety of opinion exists regarding the mechanism of the delignification of wood by the sulphite process, and that there is, as yet, insufficient experimental evidence to verify any single theory. After presenting the experimental results in the present work, the possible mechanism and kinetics of the reaction will be discussed in detail.

EXPERIMENTAL

1. Apparatus

In this investigation all cooks were carried out with wood-meal in small, sealed, bomb digesters of 100 to 200 cc. capacity, which will be described in detail later. The charged bombs were dropped into well stirred glycoline baths, preheated a few degrees above the desired temperature to offset the cooling effect of the bombs. The temperature was then held constant throughout the cook, and the bombs were removed and quenched in water at suitable intervals.

Two oil baths were used; a large one 9 x 18 x 22 inches high, and a small one made from a 3 gallon pail. Both oil baths were electrically heated. The large bath was hand controlled by an external variable resistance to 0.5°C. during the investigations reported in Part I. A mercury thermoregulator was installed for subsequent work which held the temperature constant to 0.2°C. The small bath was used for low temperature cooks and was thermostated to 0.1°C. by means of a mercury thermoregulator. In all cases adjustments were made so that the desired cooking temperature lay midway between the upper and lower limit of the variation. Hence the average temperature was always more accurate than the sensitivity of the thermostat.

2. The Preparation of Raw Materials and Treatment of Products

Well seasoned white spruce, and jack pine heartwood were the only woods used in this work. The wood was first passed through a mechanical grinder and then screened. Only the portion which passed a 40 mesh sieve and was retained on a 100 mesh sieve was used. For the investigations reported in Part II, and for a few of the experiments in Part I, the wood-meal was resin extracted in a Soxhlet apparatus for 12 hours with a mixture of alcohol and benzene (1:2).

The apparent density of the wood was determined before grinding, as the oven-dry weight over the oven-dry volume, expressed in grams per cc. The volume was measured by displacement in mercury. For a cook, 2 to 5 gram samples of the air-dry meal were weighed into each bomb and the oven-dry weight calculated from a moisture determination, made by heating a separate sample for 18 to 24 hours at 105°C.

The cooking liquor was prepared by passing sulphur dioxide gas into a suspension of a good grade of lime or magnesia in the approximate amount of water. As soon as the base was dissolved, the liquor was analyzed and diluted to give the desired concentration of combined sulphur dioxide*

---

*Note:- Total sulphur dioxide = dissolved sulphur dioxide + sulphurous acid + the bisulphite.
Combined sulphur dioxide = one half of the bisulphite.
Free sulphur dioxide = the difference between the total and the combined, all calculated as SO_2.

The total sulphur dioxide was then adjusted either by the addition of more gas, or by the application of suction. The liquor was introduced into the bombs containing the wood-meal, which were then sealed. In Part II it was found necessary to take special precautions to ensure more accurate concentrations, and these will be discussed later.

At the completion of a cook each bomb was opened, and the pulp filtered on a Buchner funnel. When sulphur determinations were to be made, the pulp was washed with 5% hydrochloric acid to remove any traces of adsorbed sulphites, which would cause an error in the analysis. In either case, the pulp was washed thoroughly with tap water, which was used in preference to distilled water, because it was found to be just hard enough to neutralize any acids still adsorbed by the pulp. If distilled water is used for washing, the pulp has a tendency to discolour or burn in the drying oven. After drying overnight at 105°C., each sample of pulp was weighed and set aside for lignin or sulphur determinations. The pulp yields are all calculated as oven-dry weight of pulp over oven-dry weight of wood, expressed in percent.

3. The Analysis of Sulphite Liquor

The iodate method of Palmrose (55) was used throughout this work for the analysis of sulphite liquor. It was found to be faster than the customary Sander and Winkler methods. Very sharp end points are obtained and the accuracy is greater, particularly with waste sulphite liquor containing a high concentration of lignin derivatives. The method is based on the following reactions:

$$KIO_3 + 3H_2SO_3 \longrightarrow KI + 3H_2SO_4$$

$$KIO_3 + 5KI + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + 3I_2$$

$$H_2SO_3 + I_2 + H_2O \longrightarrow 2HI + H_2SO_4$$

When the first reaction is completed, iodine is set free according to the second, and gives a colour with the starch indicator. This colour is not permanent as long as some sulphite remains unoxidized, because of the third reaction.

In using this method, 2 cc. of the liquor to be analyzed are pipetted into a 250 cc. Erlenmeyer containing 75 cc. of water, 2 cc. of a 1% starch-potassium iodide indicator and 3 drops of methyl red. The solution is then titrated with N/8 potassium iodate.

(a) If no lignin derivatives are present.

The blue of the starch indicator is decolourized by adding a drop of 3% sodium thiosulphate. The same solution is then titrated with N/8 sodium hydroxide to the methyl red end point. The percent total sulphur dioxide is equal to 0.2 times the number of cc. of N/8 potassium iodate; the percent free sulphur dioxide is equal to 0.2 times the number of cc. of N/8 sodium hydroxide; the percent combined sulphur dioxide is obtained by difference.

(b) If lignin derivatives are present.

After titrating with potassium iodate, the blue of the starch indicator is not decolourized with sodium thiosulphate, but the solution is titrated directly with N/8 sodium hydroxide. The alkali sets free a small amount of "reversible" sulphur dioxide, which decolourizes the starch. After the methyl red end point is reached, 2 cc. of dilute sulphuric acid are added and the solution again titrated with N/8 potassium iodate. A small correction is made for the reversible sulphur dioxide by subtracting 0.1 times the number of cc. of N/8 potassium iodate added the second time, from the apparent percent free, to obtain the correct value. The percent total and combined sulphur dioxide are calculated as before.

4. The Determination of Lignin

Except where otherwise stated, all of the lignin determinations in this investigation were made by the Ross-Potter method (57), developed in these laboratories. This method has received some criticism since it does not agree exactly with the 72% sulphuric acid method, as adapted by the United States Forest Products Laboratories, Madison (8). With hardwoods the Ross-Potter method gives somewhat lower results than the Madison method, and with conifers it gives somewhat higher results. This discrepancy is reduced, according to Phillips (56), if the wood is first extracted with alcohol-benzene, since the resin present in conifers tends to follow the lignin fraction in the determination. For this reason, all of the wood-meal used in Part II was resin extracted.

The advantage of the Ross-Potter method is the great saving in time, which is important when a large number of determinations are required, as in the present work. Because of the uncertainty regarding the structure and homogeneity of lignin, there is really little evidence to show that either one method gives a more correct value than the other. Good checks can be obtained with the Ross-Potter method, provided the same procedure is carefully followed each time. Since some of the original directions were slightly modified, a detailed description of the procedure will be given.

About 0.4 to 1.0 gram (depending on the approximate lignin content) of oven-dry wood-meal or pulp is wetted in a 250 cc. beaker with 10 cc. of commercial formaldehyde solution. After 5 minutes, 10 cc. of 72% sulphuric acid are added slowly. The beaker is placed in cold water to prevent heating and the mixture is continually stirred. After another 5 minutes, 15 cc. of concentrated sulphuric acid are added slowly with constant stirring. It is important that the acid is not allowed to become warm, as there is a tendency under such conditions for certain polysaccharides in the wood to be rendered insoluble, and to be estimated along with the lignin.

The mixture is allowed to stand until all the wood or pulp has completely dissolved. This may require from ten minutes to two hours, depending on the state of division and hardness of the pulp. Occasional stirring or maceration of the particles is advantageous. When solution is complete, 50 cc. of a mixture of glacial acetic acid and chloroform (6:1) are added, and the whole poured into a 600 cc. beaker containing 400 cc. of water. The first beaker is carefully rinsed with water and the washings added to the second.

In this manner the lignin is reprecipitated together with some carbohydrate material. The latter is hydrolysed and dissolved by heating on the steam bath for about two hours. The particles of lignin are allowed to settle over night and then filtered by suction in a weighed gooch crucible containing an asbestos mat. The precipitate is washed with 200 cc. of approximately 5% hydrochloric acid. The crucible containing the lignin is then dried for at least 3 hours at 105°C. and weighed in a glass-stoppered weighing bottle. The percent lignin in the pulp is calculated directly, and multiplying this figure by the yield of pulp gives the lignin remaining as percent of the original wood (sometimes called the "residual lignin").

The action of the formaldehyde, according to Ross and Potter, is in preventing resinification of the lignin which ordinarily occurs in sulphuric acid, by blocking the point in the lignin molecule where condensation might take place. The purpose of the chlroform-acetic mixture is to coagulate the lignin and make it easier to filter. In the majority of determinations, filtration required only 15 to 20 minutes, although occasionally one would be encountered which required several hours. This was particularly true with pulps cooked at low temperatures.

5. The Determination of Sulphur in Pulp.

The method used for the determination of sulphur in pulps was an adaption of that described by Wolensky (72) for determining sulphur in rubber. A 1 gram sample of oven-dry pulp is placed in a 500 cc. Erlenmeyer, and 5 cc. of distilled water and 10 cc. of concentrated nitric acid are added. The flask is heated gently for about half an hour, until brown fumes cease to escape. Then 5 cc. of perchloric acid are added and the heating continued until dense white fumes appear. The pulp should be completely dissolved at this point.

After the addition of 5 cc. of concentrated hydrochloric acid, the solution is heated until white fumes appear again, and then it is washed into a 250 cc. beaker. It is then diluted to 100 cc., heated to boiling and 5 cc. of 5% barium chloride solution added. The precipitated barium sulphate is allowed to settle over night, filtered on an ashless paper, ignited on a tared porcelain crucible and weighed. From the weight of barium sulphate, the percent sulphur in the pulp and in the lignin can be calculated.

PART I

The Effect of Pretreating Wood in Aqueous Solutions on Subsequent Delignification in Sulphite Liquor

PART I

The Effect of Pretreating Wood in Aqueous Solutions on Subsequent Delignification in Sulphite Liquor

INTRODUCTION

Sutherland (68) observed that heating wood in water at 70°C., caused a permanent increase in the rate of penetration of liquids through the wood. However, when an attempt was made to improve the penetration of sulphite liquor into chips in a commercial digester by a preliminary steaming, a decrease in the rate of cooking resulted.

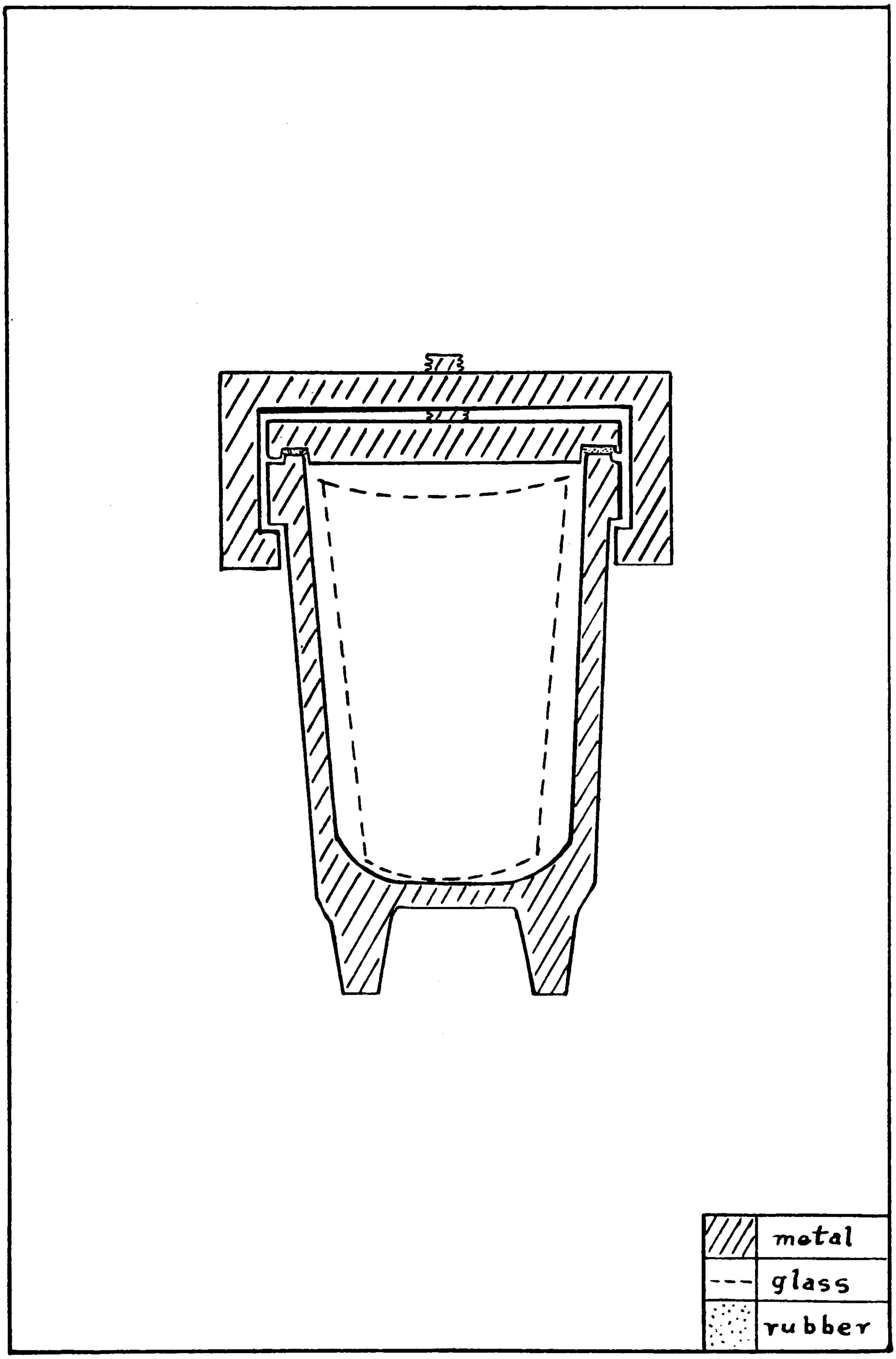
Corey (15) commenced the elucidation of this phenomenon, as already mentioned. He showed that the effect of pretreatment on subsequent delignification was not due to heating alone, but was related to the hydrogen ion concentration of the pretreating solution, and was a minimum at about pH 5. When wood was pretreated in distilled water, it was believed that sufficient acid was liberated from the wood to produce the effect. Corey found that pretreated wood could be delignified, if cooked for a longer time, and suggested that the pretreatment caused an agglomeration of the lignin which slowed up, but did not stop subsequent cooking.

The investigation of this phenomenon has been continued and extended in the present work. It should be pointed out that the pretreatment of wood, as it is described here, has no connection whatever with various methods of wood pretreatment suggested to improve commercial pulping. In every case, delignification was retarded, not improved. However, it was important to determine the cause and nature of this behaviour for practical as well as theoretical reasons. Particular interest lay in a possible connection with so-called, "burning", which sometimes occurs in a sulphite digester.

EXPERIMENTAL

Throughout Part I, all pretreatments and cooks were carried out in the 200 cc. metal digesters illustrated in Fig. 1. For acid pretreatments and sulphite cooks, bronze digesters were used; for alkali pretreatments and the one alkali cook, iron digesters were used. Both were identical in design and were covered with a lid, sealed tight by means of a rubber gasket and a clamp. Glass liners covered with watch glasses were placed inside the bronze bombs, because of the tendency of the bronze to be attacked in acid solutions and contaminate the pulp. About 4 grams of wood-meal of known moisture content were weighed into each bomb, and the pretreating solution poured inside and outside the glass liner. Each bomb was sealed, dropped into the oil bath for a definite time at constant temperature, and then quenched in cold water.

The pretreated wood-meal was filtered, washed carefully with distilled water and air-dried over night. It was then replaced in the bomb and cooked according to a definite



J.M.C. 14/3/38.

Fig. 1. The 200 cc. glass lined, bronze or iron digester

procedure, usually 3 hours at 140°C. in calcium base sulphite liquor containing 1.2% combined and 5.1% total sulphur dioxide. Since the capacity of the glass liners was 120 cc., the liquor to wood ratio was about 30:1. After cooking,the pulp was removed, filtered, washed with 5% hydrochloric acid followed by tap water, and then treated as previously described.

RESULTS AND OBSERVATIONS (PART I)

A. The Pretreatment of Wood in Buffer Solutions

1. The Effect of Temperature and pH of Pretreatment on Subsequent Delignification

A preliminary experiment to show the effect of the pH of the pretreating solution in retarding subsequent delignification was carried out to serve as a comparison for other work. Samples of spruce wood-meal were heated in McIlvaine's buffer solutions for 6 hours at 130°C., followed by cooking in sulphite liquor for 3 hours at 140°C. The results are listed in Table 1 and plotted in Fig. 2, and fully substantiate the report of Corey and Maass (17). Both the yield and lignin curves exhibit the same minimum at about pH 5. However, even where the effect of pretreatment is least, the lignin content is still considerably greater than in the case of untreated wood cooked under identical conditions.

The effect of temperature of pretreatment at pH 3, 5 and 7, on subsequent delignification was investigated between 100° and 140°C. The data are given in Table 2, and plotted in Fig. 3. In every case the effect increases rapidly with the temperature of pretreatment. The curves are in the relative order that would be expected from the variation of pH shown in Fig. 2.

TABLE 1

The Effect of pH of Pretreatment on Subsequent Delignification

Wood:- spruce meal, 40-100 mesh. Density 0.39, lignin 30.9%.

Pretreatment:- 6 hr., 130°C., McIlvaine's buffer solution.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide.
(Calcium base).

pH of pre-treating solution	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of original wood
A. Run No. 10. Untreated.				
-	48.9	47.1	3.71	1.82
B. Run Nos. 2, 3, 7. Pretreated.				
2.2	64.0	47.7	25.4	16.3
3.0	57.0	47.5	16.4	9.46
4.0	53.4	47.9	10.3	5.50
4.6	52.6	47.9	8.90	4.68
5.0	53.2	48.8	8.29	4.41
6.0	57.0	51.7	9.22	5.26
7.0	58.9	52.4	10.9	6.45

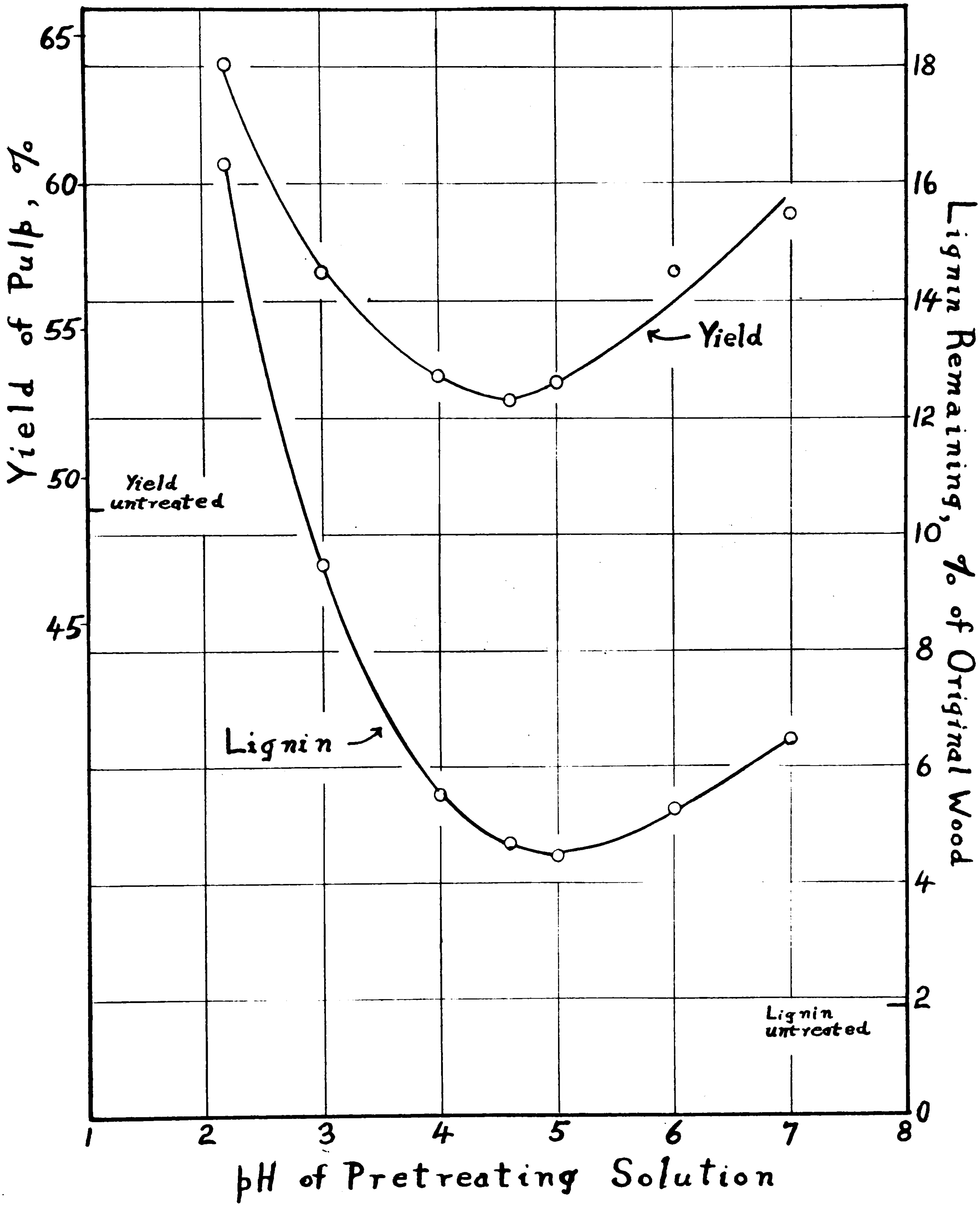


Fig. 2. The effect of pH of pretreatment on subsequent delignification

TABLE 2

The Effect of Temperature of Pretreatment on Subsequent Delignification

Run No. 7.

Wood:- spruce meal, 40-100 mesh. Density 0.39, lignin 30.9%.

Pretreatment:- McIlvaine's buffer solution, 6 hr.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

pH of pre-treating solution	Temp. of pre-treatment, °C.	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of original wood
3	100	49.8	47.0	5.64	2.81
	110	50.0	46.7	6.69	3.34
	120	53.2	47.4	11.0	5.84
	130	57.0	47.5	16.6	9.46
5	100	49.2	46.9	4.77	2.35
	110	49.8	47.5	4.60	2.29
	120	52.4	48.5	7.47	3.91
	130	55.1	49.3	10.35	5.81
	140	58.9	50.3	14.6	8.60
7	100	53.0	49.9	5.83	3.09
	110	54.1	50.0	7.58	4.10
	130	60.1	52.6	12.4	7.40
	140	64.6	52.6	18.6	12.0

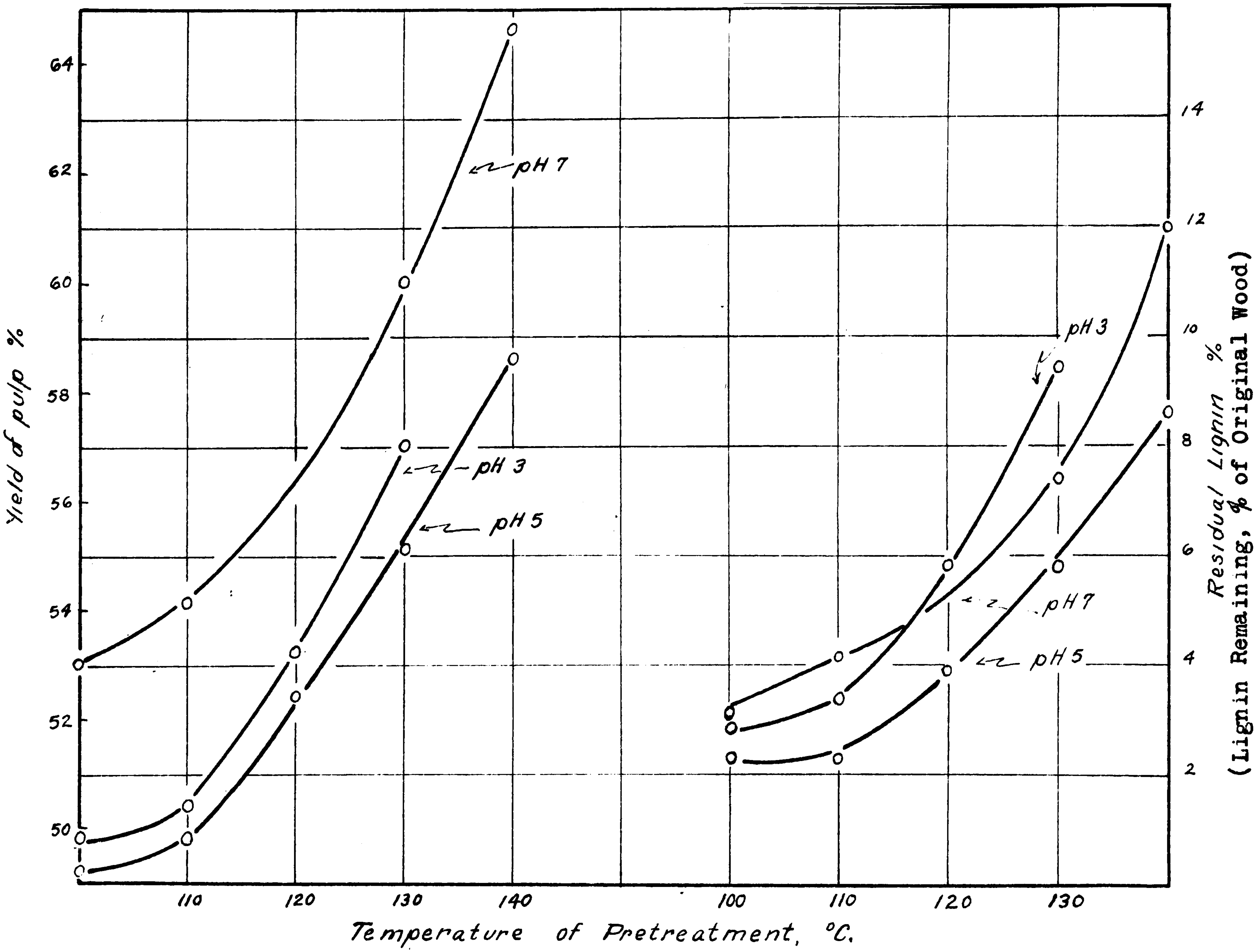


Fig. 3. The effect of temperature of pretreatment on subsequent delignification

A comparison of Tables 1 and 2, shows that wood pretreated at 100°C. is cooked almost as much as untreated wood. It therefore seems probable that pretreatment below 100°C. has little, if any, harmful effect unless carried out too long or in too acid a solution. No explanation can be given for the crossing of the lignin curves for pH 3 and pH 5. Duplicate runs were made at 100° and 110°C. for pH 3, which agreed well with those recorded. It was not considered important enough to investigate further.

2. The Effect of Time of Pretreatment on Subsequent Delignification

In the preceding experiments the time of pretreatment was only 6 hours, and it was desired to determine the change in cooking properties of wood with increase in the time of pretreatment. The first series was pretreated at pH 3, 130°C. for periods up to 48 hours, followed by the same 3 hour cook at 140°C.

The results are shown in Table 3 and Fig. 4. It is observed that the pretreating effect, as evinced by the yield and lignin curves, increases rapidly at first and then more slowly. However, even after 48 hours pretreatment, the slope of the lignin curve indicates that the effect has not reached a maximum. The ratio of sulphur to lignin in the pulps after the same length of cook, decreases with increase in the time of pretreatment This may be caused either by a decrease in the rate of sulphonation of the lignin due to

TABLE 3

The Effect of Time of Pretreatment on Subsequent Delignification

Run Nos. 7, 8, 9, 12.

Wood:- spruce meal, 40-100 mesh. Density 0.39, lignin 30.9%.

Pretreatment:- McIlvaine's buffer solution, pH 3, 130°C.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide.
(Calcium base).

Time of pretreatment, hours	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of original wood	Sulphur, % of pulp	Sulphur, % of lignin
0	48.8	47.3	3.16	1.54	0.40	12.5
6	57.0	47.5	16.6	9.46	1.19	7.2
12	64.3	48.4	24.7	15.9	1.26	5.10
18	65.9	47.8	27.4	18.1	1.34	4.92
24	66.7	46.9	29.7	19.8	1.36	4.57
48	67.3	43.4	35.5	23.9	1.08	3.05

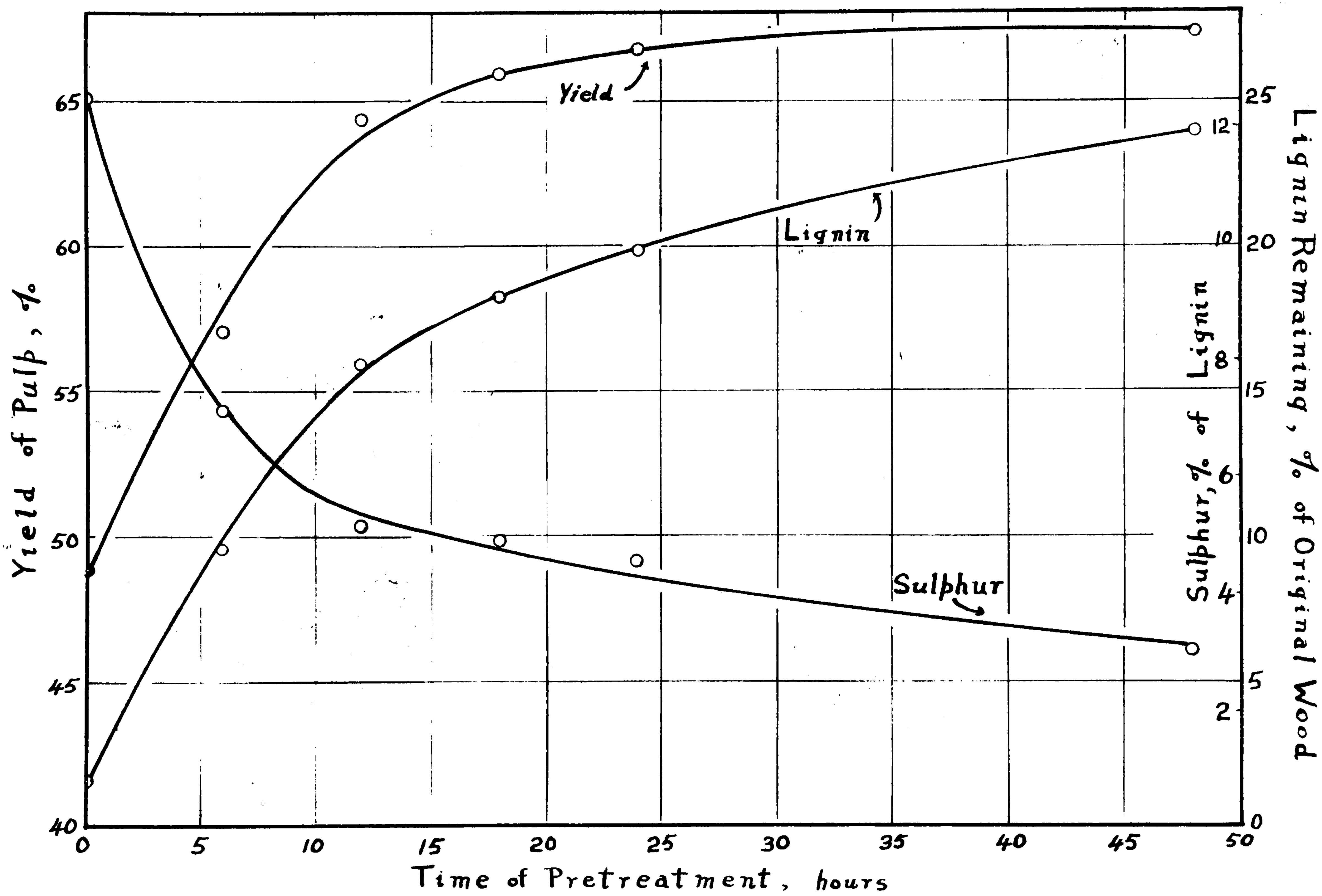


Fig. 4. The effect of time of pretreatment (pH3, 130°C.) on subsequent delignification

TABLE 4

The Effect of Time of Pretreatment on Subsequent Delignification

Run Nos. 13, 16.

Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.

Pretreatment:- McIlvaine's buffer solution, pH 7.01 before pretreatment; 130°C.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Time of pre-treatment, hours	pH of solution after pre-treatment	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin % of original wood
0	-	48.3	47.0	2.58	1.25
2	6.94	56.2	52.0	7.48	4.21
5	6.87	60.9	53.6	11.9	7.25
8	6.87	62.5	53.6	14.3	8.94
12	6.87	66.0	54.8	17.0	11.2
18	6.83	66.2	51.8	21.7	14.4
24	6.80	68.4	52.7	23.0	15.7

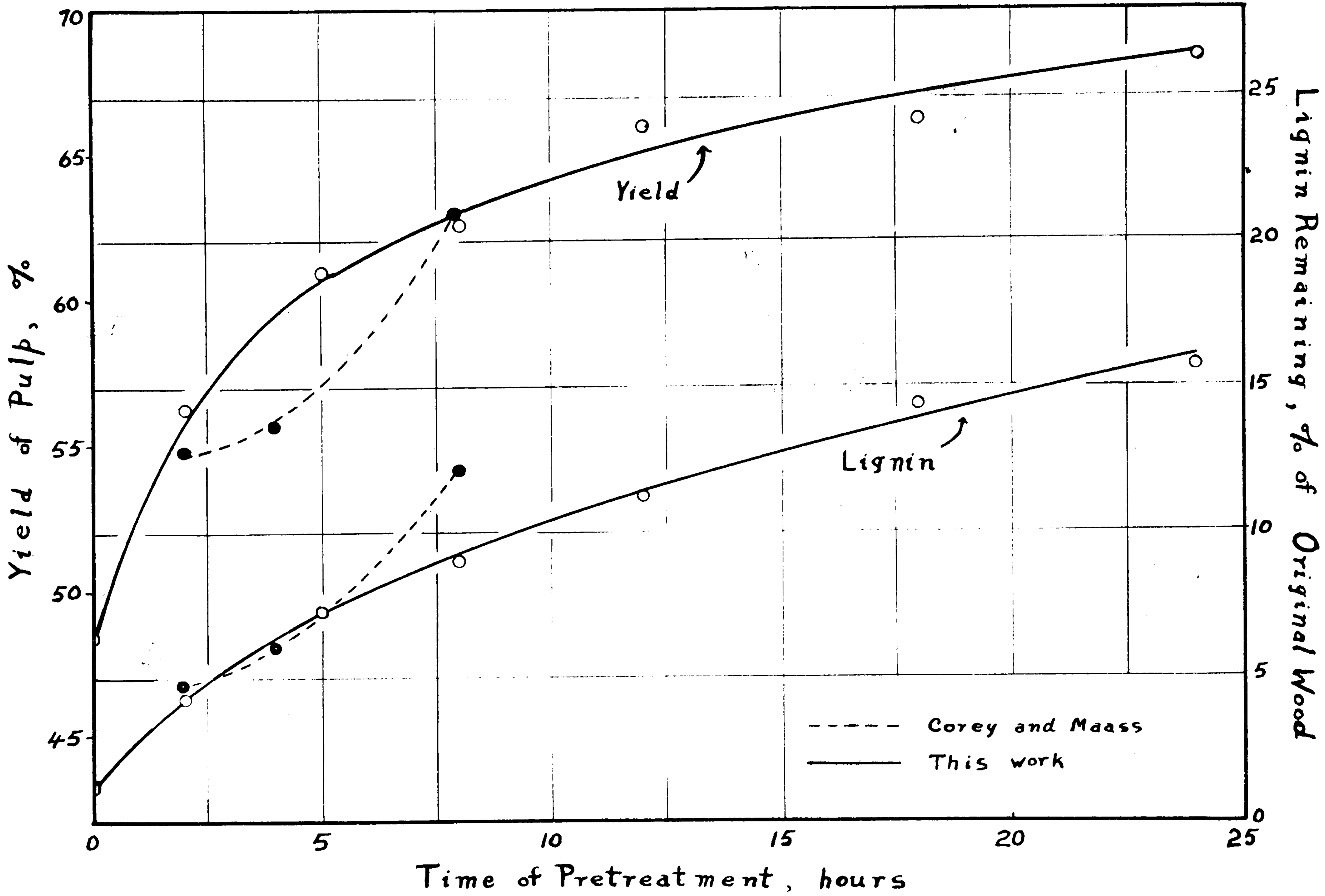


Fig. 5. The effect of time of pretreatment (pH 7, 130°C.) on subsequent delignification.

pretreatment, or a decrease in the rate of removal of sulphonated lignin.

Before increasing the severity of the pretreatment still further, a series was first pretreated at pH 7, 130°C. for periods up to 24 hours, in order to check some anomalous results reported by Corey and Maass (17). The data are recorded in Table 4 and compared with those of Corey and Maass in Fig. 5. The curves obtained in the present work are essentially the same shape as those at pH 3 (Fig. 4), differing in magnitude as would be expected from the difference in the pH of pretreatment, as shown in Fig. 2. The curves of Corey and Maass can only be attributed to experimental error since it is unreasonable to suppose that the effect of pretreatment would accelerate with increase in time. In the above series the pH of the solution after pretreatment was determined by means of a quinhydrone electrode. Table 4 shows that the pH of the buffer at room temperature was altered very little by the acids released from the wood during pretreatment.

The next series was pretreated at pH 3 and 140°C. in order to shorten the time required. The data are listed in Table 5. The yeilds of pulp, lignin and non-lignin are plotted in Fig. 6, and the sulphur as percent of pulp and percent of lignin is plotted in Fig. 7, against the time of pretreatment. The latter is similar to the sulphur curve in Fig. 4. The yield of non-lignin or carbohydrate decreases

TABLE 5

The Effect of Time of Pretreatment on Subsequent Delignification

Run Nos. 13, 14, 15, 17.

Wood:- spruce meal, 40-100 mesh. Density 0.34. Ross-Potter lignin 29.0%, Madison lignin 26.3%.
Pretreatment:- McIlvaine's buffer solution, pH 3, 140°C.
Cooking:- Bronze bombs, 3 hr., 140°C.
Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Time of pretreatment, hours	Yield of pulp, %	Yield of non-lignin, %	Ross-Potter lignin, % of pulp	Ross-Potter lignin, % of original wood	Madison lignin, % of pulp	Madison lignin, % of original wood	Sulphur, % of pulp	Sulphur, % of Ross-Potter lignin
0	48.3	47.0	2.58	1.25	-	-	0.33	13.4
6	61.9	50.0	19.2	11.9	-	-	1.18	6.15
18	66.8	45.1	32.5	21.7	31.8	21.3	1.21	3.73
24	66.8	43.9	34.2	22.9	-	-	1.20	3.50
48	67.8	39.6	41.5	28.2	35.3	23.9	1.08	2.61
62	69.0	39.0	43.6	30.0	-	-	0.95	2.17
72	70.4	37.8	46.2	32.6	-	-	1.10	2.39
96	70.2	36.2	48.4	34.0	39.9	28.1	0.80	1.65

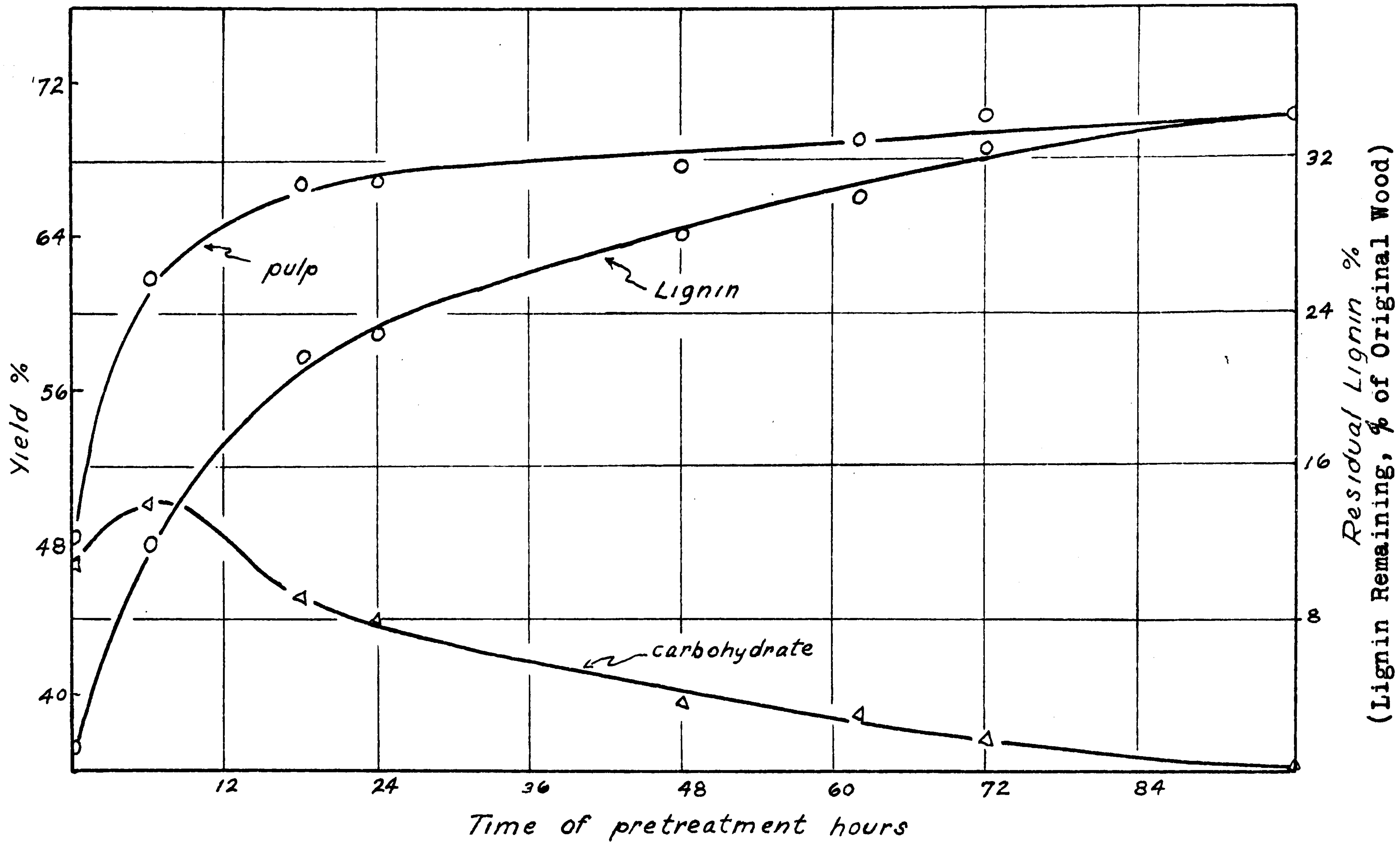


Fig. 6. The effect of time of pretreatment (pH 3, 140°C.) on subsequent delignification.

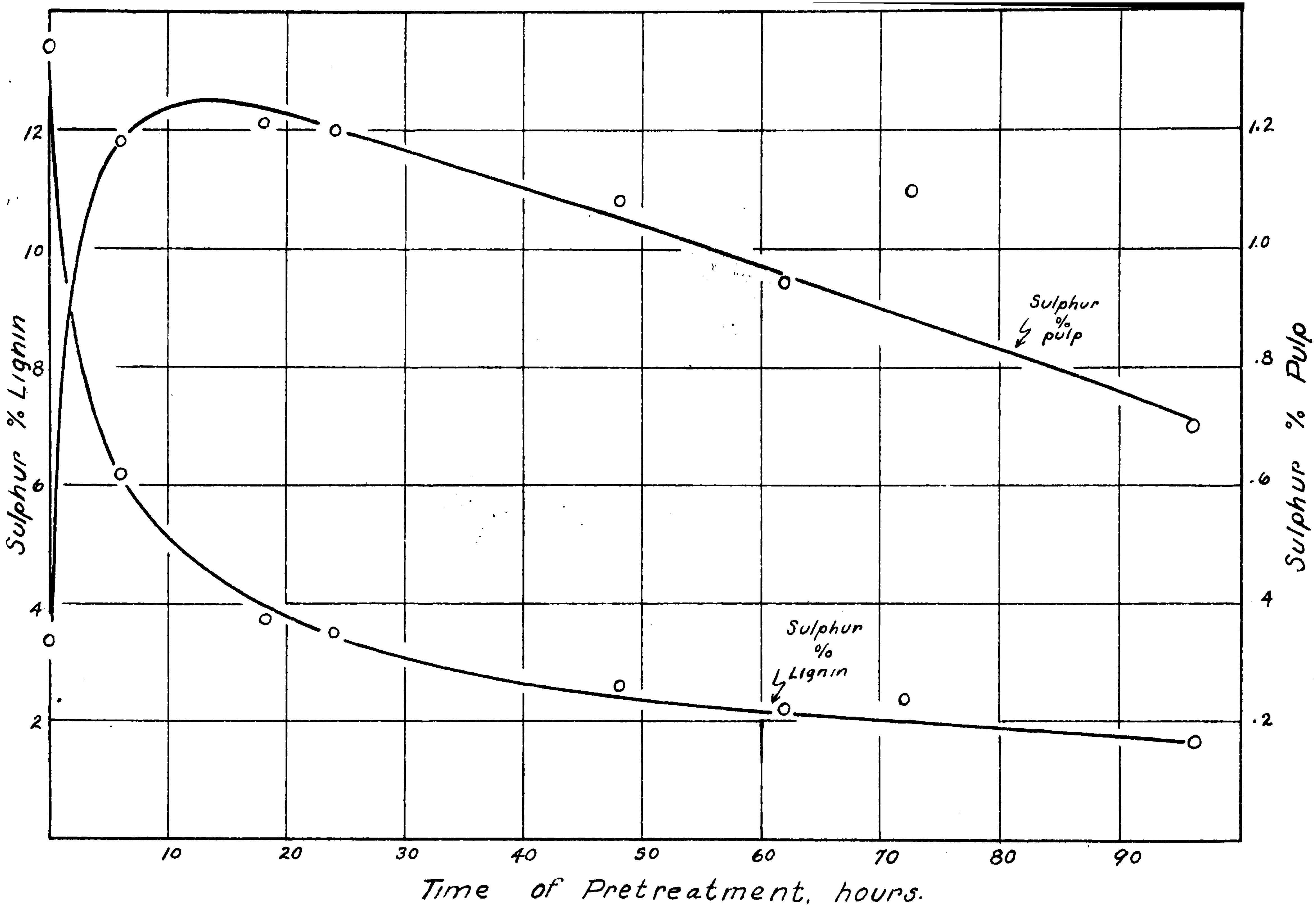


Fig. 7. The variation in the degree of sulphonation with the time of pretreatment (pH 3, 140°C.).

steadily with increase in the time of pretreatment, as would be expected from the mild hydrolysis of wood.

An examination of the lignin curve in Fig. 6, is of much greater interest. It is observed that after about 55 hours pretreatment and 3 hours cooking, the Ross-Potter lignin remaining in the pulp, calculated as percent of the original wood, is equal to the original lignin content of the wood before treatment (29.0%). That is, apparently no lignin whatever has been removed in three hours cooking. In addition, the residual lignin continues to increase so that after 96 hours pretreatment followed by 3 hours cooking, there is 5% more lignin present than in the original wood.

The first explanation that occurred was that the Ross-Potter method of lignin analysis might be in error. Therefore the three samples pretreated 18, 48 and 96 hours followed by 3 hours cooking, were analyzed by the Madison method. These values are also given in Table 5, and it is observed that the Madison method gives somewhat lower results than the Ross-Potter method, as expected. However, in the case of the 96 hour sample the lignin is still 2% higher than the Madison lignin content of the original wood (26.3%). Evidently some substance is formed in the wood during the pretreatment which is estimated as "apparent lignin" even by the Madison method. This point required further investigation.

3. The Formation of Apparent Lignin

To determine the extent of this apparent lignin formation during the pretreatment, samples of wood-meal were again heated in solutions of pH 3 at 140°C. for periods up to 96 hours, but were not cooked afterwards in sulphite liquor. The yield, the Ross-Potter lignin and the Madison lignin content of the wood-meal so treated was determined, and is reported in Table 6 and Fig. 8.

It is observed that both the Ross-Potter and Madison lignins, expressed as percent of the original wood, increase in a regular manner with the time of treatment. The two dotted lines in Fig. 8 represent the original lignin content of the wood as determined by each method of analysis. The difference between these lines and the corresponding lignin curves for treated but uncooked wood-meal, gives the amount of apparent lignin formed during the pretreatment. By subtracting this amount from the lignin remaining after a subsequent three hours cooking, a corrected lignin value is obtained. These corrected values from Table 5 are given in Table 9, and plotted in Fig. 8.

After the correction for the apparent lignin is made, it can be seen that none of the original lignin is removed from the wood after 96 hours pretreatment and 3 hours cooking. This statement holds, irrespective of which method was used to determine the lignin. A comparison of Tables 5 and 6 also shows that none of the apparent lignin formed during the 96 hours pretreatment is removed during subsequent cooking.

TABLE 6

The Effect of Time of Treatment on the Formation of Apparent Lignin

Run No. 22.

Wood:- spruce meal, 40-100 mesh. Density 0.34.

Treatment:- McIlvaine's buffer solution, pH 3, 140°C.

Time of treatment, hours	Yield after treatment, %	Yield of non-lignin, %	R.-P. lignin, % of treated wood	R.-P. lignin, % of orig. wood	Madison lignin, % of treated wood	Madison lignin, % of orig. wood
0	100	71.0	29.0	29.0	26.3	26.3
12	74.4	44.3	40.5	30.1	35.9	26.7
24	72.5	41.7	42.4	30.8	-	-
48	71.5	39.8	44.3	31.7	38.2	27.3
72	71.3	38.3	46.3	33.0	-	-
96	71.3	37.3	47.7	34.0	40.1	28.6

TABLE 7

The Effect of pH of Treatment on the Formation of Apparent Lignin

Run No. 26.

Wood:- spruce meal, 40-100 mesh. Density 0.34; Ross-Potter lignin, 29.0%.

Treatment:- McIlvaine's buffer solution, 48 hr., 140°C.

pH of treating solution	Yield after treatment, %	Yield of non-lignin, %	R.-P. lignin, % of treated wood	R.-P. lignin, % of orig. wood
2.2	66.8	33.4	50.0	33.4
5.0	85.2	53.2	37.6	32.0
8.0	82.6	52.5	36.5	30.1

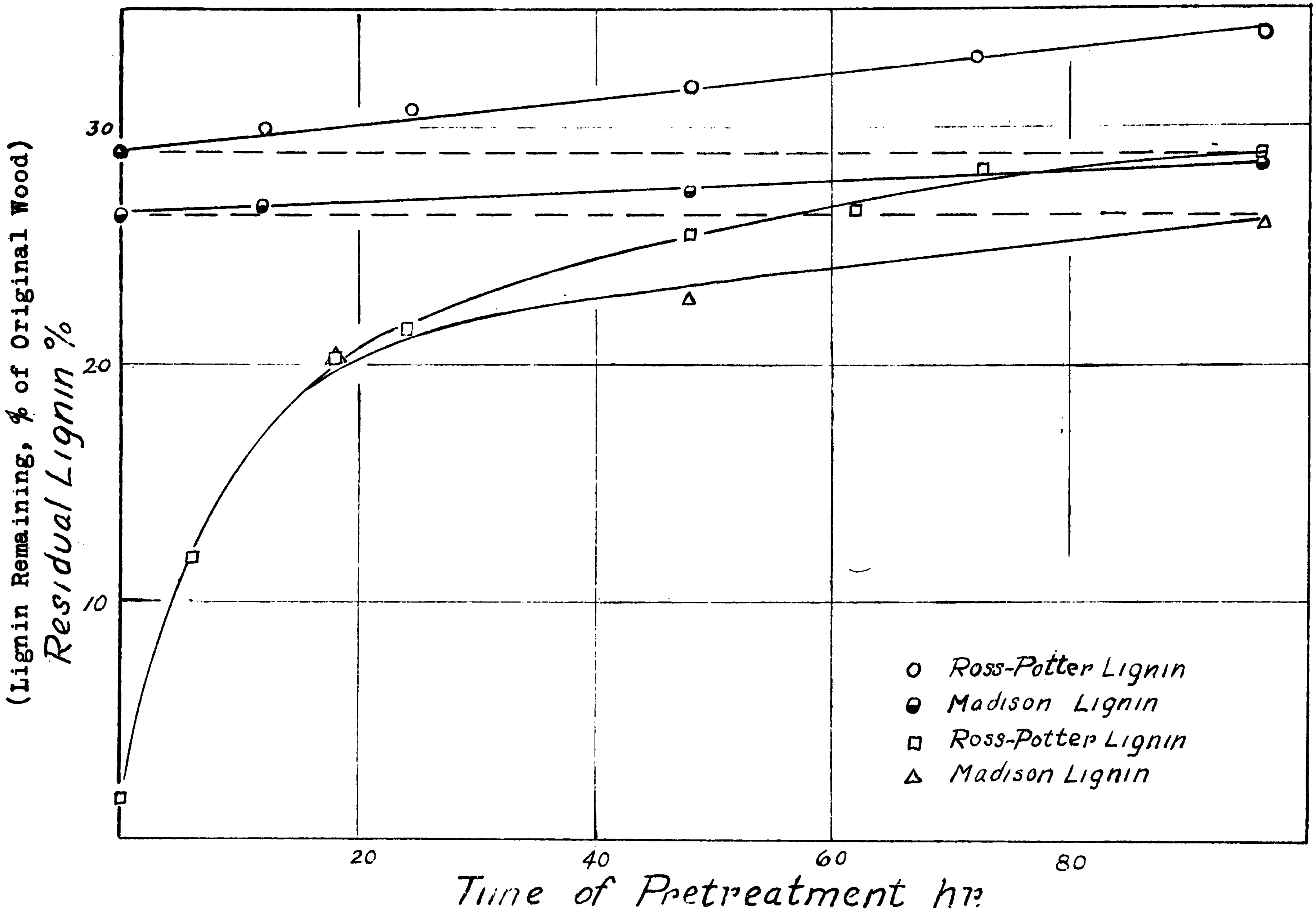


Fig. 8. The effect of time of pretreatment (pH 3, 140°C.) on the formation of apparent lignin.

TABLE 8

The Effect of Treatment on Cotton Cellulose

Run No. 17.
Material:- unpurified cotton cellulose; apparent lignin, 0.35%.
Treatment:- McIlvaine's buffer solution, 72 hr., pH 3, 140°C.

Yield after treatment, %	Yield of non-lignin, %	Apparent lignin, % of treated cellulose	Apparent lignin, % of original cellulose
93.3	93.1	0.24	0.22

TABLE 9

The Effect of Time of Pretreatment on Subsequent Delignification

(Corrected values from Table 5)

Time of pretreatment, hours	Yield of pulp, %	Yield of non-lignin, %	R.-P. lignin, % of pulp	R.-P. lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of R.-P. lignin
0	48.3	47.0	2.58	1.25	0.33	13.4
6	61.9	50.2	18.8	11.7	1.18	6.28
18	66.8	46.1	30.9	20.7	1.21	3.91
24	66.8	45.2	32.3	21.6	1.20	3.71
48	67.8	42.2	37.8	25.6	1.08	2.86
62	69.0	42.3	38.7	26.7	0.94	2.44
72	70.4	41.8	40.6	28.6	1.10	2.71
96	70.2	41.2	41.3	29.0	0.80	1.93

The correction for the apparent lignin after 6 hours pretreatment is negligible, so that previous results are not in error.

A few experiments were made to determine the effect of pH of treatment on the formation of apparent lignin, and the results are shown in Table 7. The amount of apparent lignin formed increases with the acidity of the solution. To prove that cellulose was not the precursor of the apparent lignin, a sample of cotton cellulose was heated at pH 3, 140°C., for 72 hours. Table 8 shows that no apparent lignin was formed.

4. The Pretreatment of Jack Pine Heartwood

In order to show that the pretreatment phenomena were not peculiar to spruce, a few experiments were made with jack pine heartwood-meal. Since the cooking of jack pine by the sulphite process is rendered difficult by the presence of resins, it was necessary to first determine the effect of solvent extraction on the cooking of jack pine as compared with spruce.

Table 10, A shows that little, if any, change in the cooking properties of untreated spruce wood is produced by a preliminary solvent extraction. Spruce wood extracted after pretreatment does not cook any better than unextracted, pretreated wood (Table 10, B). However, resin extraction does greatly increase the rate of cooking of untreated jack pine (Table 10, C). Unextracted jack pine is comparatively difficult to delignify but extracted jack pine cooks almost as well as spruce.

TABLE 10

The Effect of Resin Extraction on the Cooking of Untreated and Pretreated Spruce and Jack Pine

Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%. jack pine heartwood meal, 40-100 mesh. Density 0.41, lignin 32.6%.

Extraction:- Soxhlet 12 hr., alcohol-benzene (1:2).

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Treatment	Loss on extraction, %	Lignin before cooking, % orig. wood	Yield of pulp, % original wood	Yield of non-lignin, % orig. wood	Lignin, % of pulp	Lignin, % of orig. wood
A. Run No. 13. Spruce, untreated.						
unextracted	-	29.0	48.3	47.0	2.58	1.25
extracted	3.66	26.7	47.3	46.1	2.46	1.17
B. Run Nos. 19, 21. Spruce, pretreated 36 hr., pH 3, 140°C.						
unextracted	-	33.9	69.0	46.5	32.6	22.5
extracted after pretreatment	4.20	30.4	68.8	46.8	32.0	22.0
C. Run No. J-7. Jack pine, untreated.						
unextracted	-	32.6	53.4	46.0	13.8	7.36
extracted	4.75	27.0	46.1	44.4	3.76	1.73

TABLE 11

The Effect of pH of Pretreatment on Subsequent Delignification of Jack Pine

Wood:- jack pine heartwood, 40-100 mesh. Density 0.41, lignin 32.6%.

Extraction:- Soxhlet 12 hr., alcohol-benzene (1:2).

Pretreatment:- McIlvaine's buffer solution, 6 hr., 130°C.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

pH of pretreating solution	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood
A. Run No. J-3, unextracted.				
2.2	66.6	42.2	36.6	24.4
3	63.9	44.3	30.7	19.6
4	60.5	45.4	25.0	15.1
5	62.1	46.8	24.6	15.3
6	64.5	48.5	24.8	16.0
8	67.6	49.6	26.6	18.0
B. Run No. J-5, extracted before pretreatment.				
2.2	60.4	43.6	27.7	16.8
3	55.4	44.6	19.5	10.8
4	50.5	44.0	12.8	6.46
5	50.8	44.9	11.6	5.90
6	54.2	47.6	12.2	6.61
8	59.1	48.5	18.0	10.6
C. Run No. J-10, extracted after pretreatment.				
3	57.8	43.3	25.2	14.5
6	57.8	46.6	19.3	11.2
8	63.8	48.1	24.6	15.7

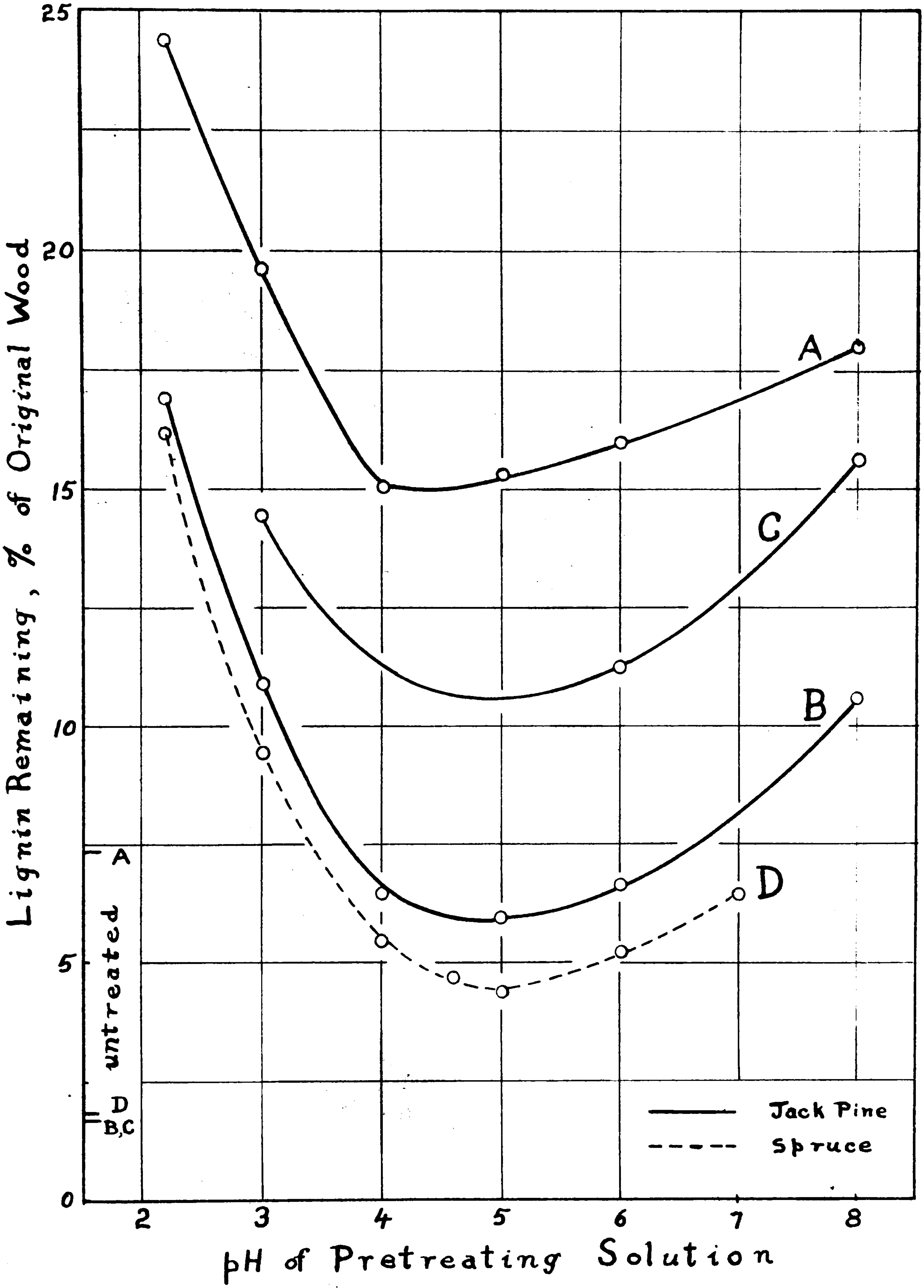


Fig. 9. The effect of pH of pretreatment on the subsequent delignification of jack pine. A and D, unextracted; B, extracted before pretreatment; C, extracted after pretreatment.

The effect of pH of pretreatment (6 hours, 130°C) on the subsequent delignification of jack pine (3 hours, 140°C.) was investigated with wood-meal unextracted, extracted before pretreatment, and extracted after pretreatment. The data are listed in Table 11, and the lignin curves are plotted in Fig. 9. The dotted lignin curve is that for spruce wood pretreated in the same manner (taken from Fig. 2) and serves as a comparison.

It is observed that pretreatment retards the delignification of jack pine in the same manner as spruce, and the pH curves all show a minimum at about pH 5. Unextracted, pretreated jack pine (Fig. 9, A) cooks much more slowly than extracted, pretreated jack pine (Fig. 9, B) or pretreated spruce (Fig. 9, D), as would be expected from the cooking properties of the untreated woods. When jack pine wood is extracted after pretreatment and then cooked, the resulting lignin curve (Fig. 9, C) lies midway between curves A and B. Possibly the resin cannot be extracted as easily after pretreatment. The important point, however, is that the lignin curves are all similar in shape and exhibit the same minimum, indicating that jack pine lignin is affected in the same manner as spruce lignin during pretreatment.

5. The Rate of Delignification of Pretreated Spruce Wood

It was considered desirable to study the rate of delignification of severely pretreated spruce wood in the hope

TABLE 12

The Rate of Delignification of Untreated Spruce Wood

Run No. 18.

Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.

Cooking:- Bronze bombs, 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Time of cooking, hours	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
0.5	82.7	61.4	25.8	21.3	0.703	2.72
1	68.7	55.0	20.1	13.7	0.967	4.81
2	54.1	49.2	9.13	4.94	0.763	8.37
3	47.4	45.9	3.12	1.48	0.331	13.4
4	45.8	45.1	1.43	0.65	0.258	18.0
5	44.4	44.0	0.90	0.40	0.208	23.1

that it would throw some light on the phenomenon, and to see if cooking for a sufficient length of time would bring about complete delignification. The rate of delignification of untreated wood-meal at 140°C., was first determined to serve as a comparison. The results are given im Table 12, and the residual lignin is plotted on a logarithmic scale in Fig. 10. Although the curve is represented here by a straight line, it

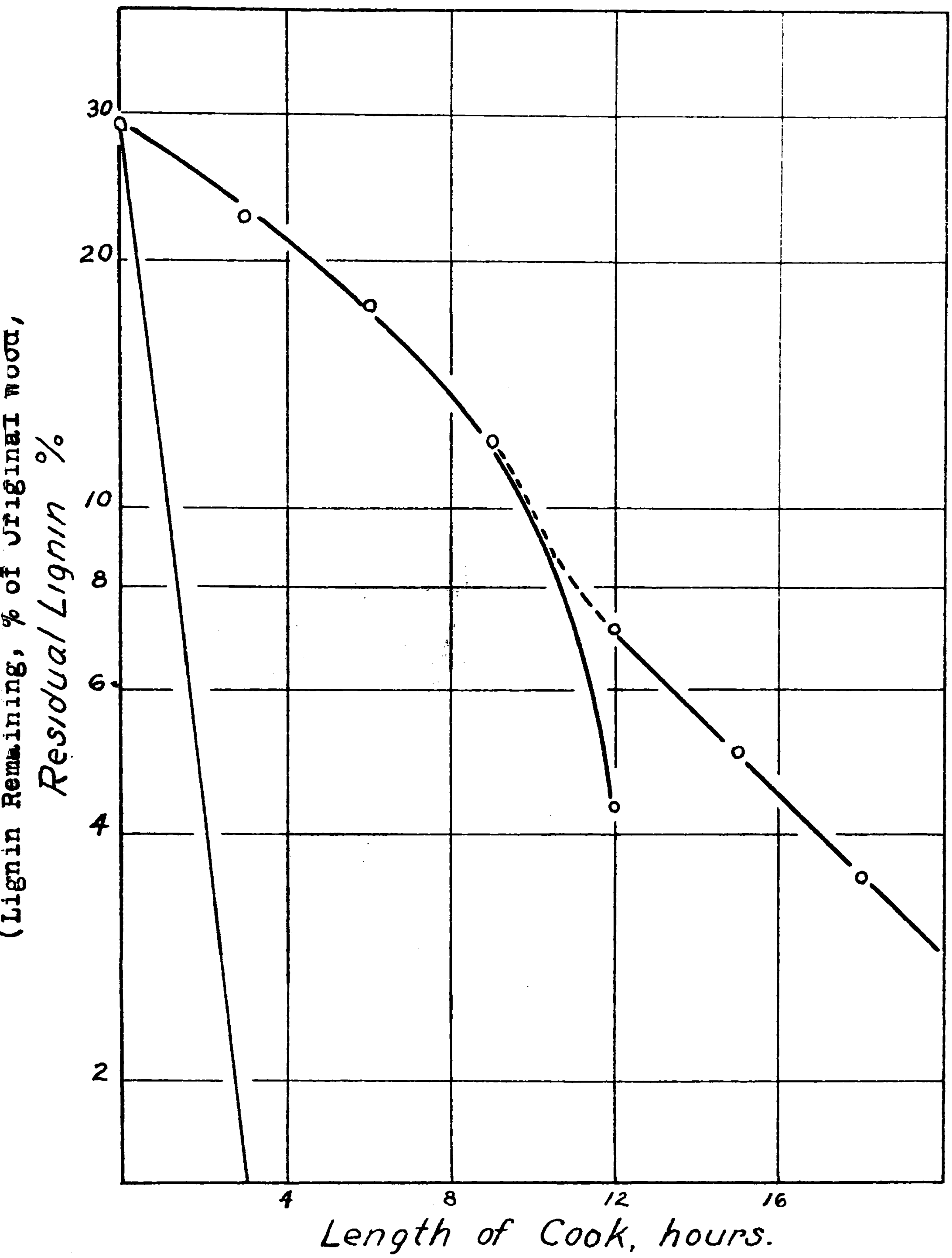


Fig. 10. The rate of delignification of untreated spruce wood and spruce wood pretreated 36 hr., pH 3, 140°C.

TABLE 13

The Rate of Delignification of Pretreated Spruce Wood

Run Nos. 19, 20.

Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.

Pretreatment:- McIlvaine's buffer solution, 36 hr., pH 3, 140°C. After pretreatment, yield 80.1%, lignin 33.8% of original wood.

Cooking:- Bronze bombs, 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Time of cooking, hours	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
3	69.0	46.5	32.6	22.5	1.21	3.72
6	62.6	45.0	28.1	17.6	1.35	4.81
9	54.6	42.7	21.8	11.9	1.56	7.14
12	46.3	42.0	9.3	4.32	1.40	15.0
9 + 3	49.9	42.8	14.2	7.08	0.76	5.35
9 + 6	47.4	42.3	10.7	5.06	0.57	5.31
9 + 9	44.3	41.4	7.85	3.52	0.41	5.18
9+12	44.0	41.6	5.98	2.63	0.31	5.26

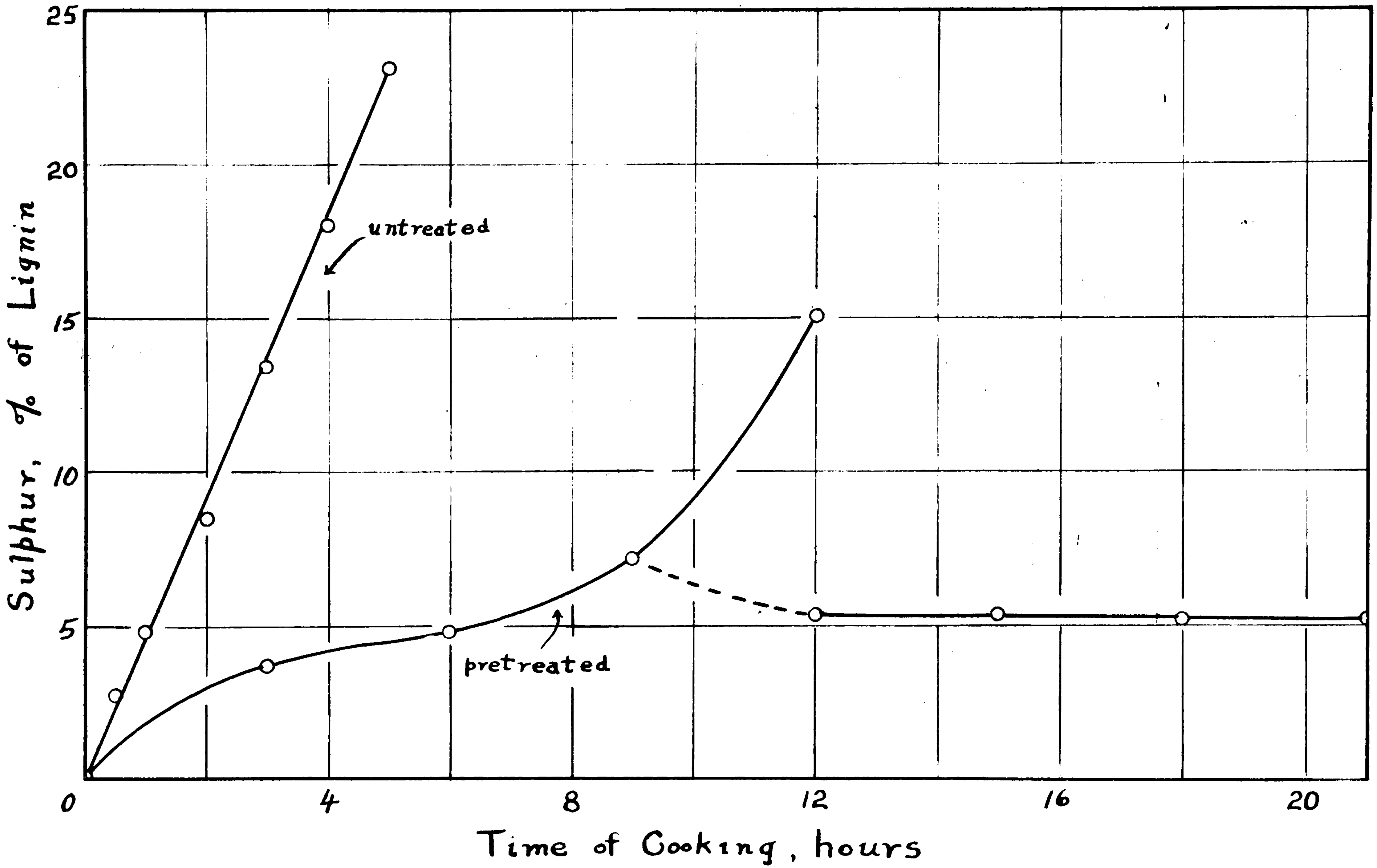


Fig. 11. The variation in the ratio of sulphur to lignin with time of cooking for untreated spruce wood, and spruce wood pretreated 36 hr., pH 3, 140°C.

is actually a reversed S-shape, which can be seen when plotted on a larger scale. This deviation from the straight line will be discussed in a later section.

A large quantity of the same wood-meal was heated in a 2 liter Allegheny metal digester in a buffer solution of pH 3 at 140°C. for 36 hours. Samples of this pretreated wood-meal were then cooked in the same sulphite liquor as the untreated wood-meal for various periods at 140°C. Unfortunately after 12 hours cooking the liquor decomposed, precipitating sulphur in the pulp and making lignin determinations impossible. However, by removing bombs after 9 hours cooking and replacing the moist pulp immediately in fresh liquor of the same initial concentration, the length of the cook was extended to 21 hours. All of the data are listed in Table 13. The delignification curve for the pretreated wood is plotted in Fig. 10. The sulphur curves for the cooking of both the untreated and pretreated woods are plotted in Fig. 11.

An examination of Fig. 10 shows that during the first stage in the cooking of the pretreated wood, the rate of delignification is much less than that of the untreated wood up to the 9th hour. However, between the 9th and 12th hour, the rate so increases that it becomes very nearly equal to that of the untreated wood. At the 12th hour the lignin content has been reduced to 4.32% of the original wood, which is a moderately cooked pulp. From the slope of the curve it would seem that the remainder of the lignin would have been rapdily removed, had not the liquor decomposed.

Fig. 11 shows that the sulphur content of the lignin increases rapidly in a linear manner with the time of cooking for the untreated wood. For the pretreated wood, this ratio of sulphur to lignin increases at a moderate rate during the first two hours of cooking, and then very slowly until the 9th hour. Between 9 and 12 hours, the degree of sulphonation increases rapidly, corresponding to the increased rate of delignification. It should be pointed out that these values of the sulphur as percent of lignin are subject to the errors of lignin analysis as well as sulphur analysis. Therefore, too much importance cannot be attached to them at low lignin values, where a small error in the lignin would cause a relatively large error in the ratio of sulphur to lignin.

With regard to the second stage of the cooking of the pretreated wood, a discontinuity in both the lignin and sulphur curves may be observed. The rate of delignification in the second stage does not increase after the 9th hour, as it does in the case of a single stage cook, but remains constant to the 21st hour. This fact appeared so unreasonable that the whole series was repeated, but exactly the same results were obtained, within the limits of experimental error. Two cooks of untreated wood were then interrupted; the first was cooled to room temperature only, and the second was replaced in fresh liquor. After further cooking neither showed any difference from a continuous cook of the same duration.

The immediate object of these experiments was to show that severely pretreated wood could be delignified. The lowest lignin value was obtained in two stages in 21 hours (2.63%), and the slope of the curve indicates that further delignification is possible. Whether there is some limit to the reversibility of the pretreatment effect and the cooking action cannot be stated. That is, can wood be so severely pretreated that it cannot be delignified with any amount of cooking? That is impossible to determine because very long cooks tend to destroy the cellulose, and a mere mechanical removal of the lignin may occur.

6. The Effect of pH of Pretreatment on the Subsequent Delignification of Spruce Wood in Sulphite Liquor

It was decided to investigate the effect of pH of pretreatment on subsequent delignification more fully for several reasons. It was of interest to extend the pH range and to try other buffers than McIlvaine's (citrate-phosphate) in case ions other than the hydrogen ion were contributing to the pretreating effect. A variety of standard buffer solutions were made up according to the directions of Britton (9) to cover the whole range pH 1 to pH 13. Samples of wood-meal were then pretreated 6 hours at 140°C., followed by 3 hours cooking at 140°C. The results are given in Table 14, and the yield, lignin and sulphur values are plotted against the pH of pretreatment in Fig. 12.

TABLE 14

The Effect of pH of Pretreatment on the Subsequent Delignification in Sulphite Liquor

Run Nos. 30, 31, 33, 44.
Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.

Pretreatment:- 6 hr., 140°C.
Cooking:- Bronze bombs, 3 hr., 140°C.
Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

pH of pretreating solution	Buffer solution	Salt conc., moles per l.	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
1	HCl, KCl	0.05	59.6	28.8	51.6	30.8	0.52	1.01
2	" "	0.05	64.0	42.2	34.1	21.8	1.12	3.28
3	McIlvaine citric ac. Na_2HPO_4	0.12	63.3	47.9	24.3	15.4	1.11	4.58
4	"	0.14	57.8	48.1	16.8	9.7	0.99	5.89
5	"	0.15	59.3	50.1	15.5	9.2	1.02	6.58
6	"	0.16	61.6	52.1	15.2	9.5	1.02	6.67
7	"	0.18	64.1	52.7	17.8	11.4	1.08	6.08
8	"	0.20	66.1	51.9	21.4	14.2	1.13	5.26

TABLE 14 (continued)

pH of pretreating solution	Buffer solution	Salt, conc., moles per l.	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
7	H_3BO_3 $Na_2B_4O_7$	0.19	57.6	48.6	15.7	9.0	-	-
8	"	0.16	61.7	51.5	16.5	10.2	-	-
9	"	0.08	68.0	52.0	23.5	16.0	-	-
8	H_3BO_3 KCl, NaOH	0.10	57.6	48.8	15.3	8.8	-	-
9	"	0.07	62.0	52.2	15.9	9.8	-	-
10	"	0.06	66.9	52.9	20.9	14.0	-	-
11	Na_2HPO_4 NaOH	0.12	68.6	52.8	23.1	15.8	1.10	4.77
12	"	0.06	67.9	50.2	26.1	17.7	1.08	4.15
13	0.1 N-NaOH	-	66.6	49.0	26.4	17.6	1.09	4.13

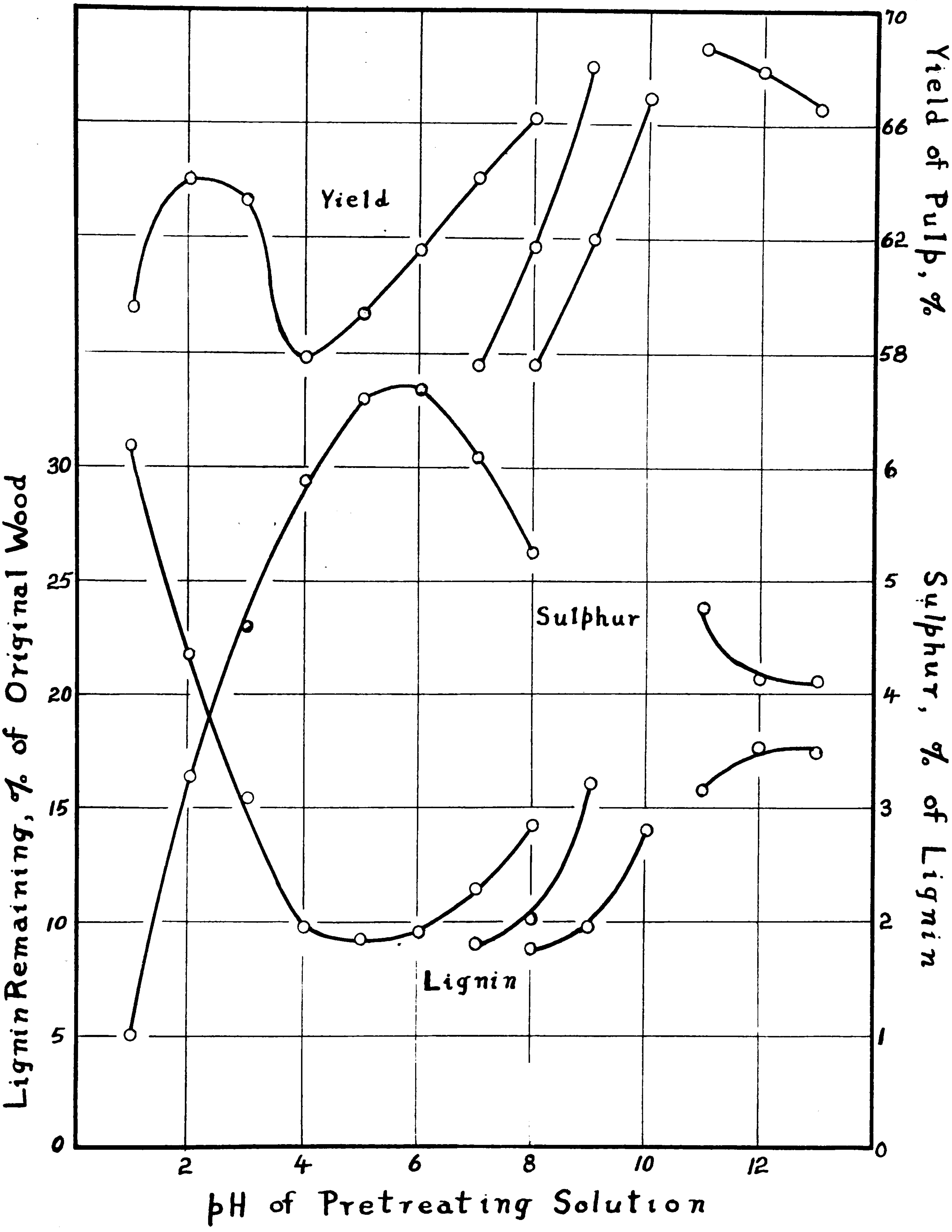


Fig. 12. The effect of pH of pretreatment on subsequent delignification in sulphite liquor.

At pH 1, it may be observed that a small amount of apparent lignin is formed, even though the pretreatment was carried out for only 6 hours. The yield of non-lignin at the same time is unusually low because of the hydrolytic action of the stronger acid on the carbohydrates during pretreatment. The lignin curve corresponding to pretreatment in the McIlvaine's buffer solution shows the same minimum at pH 5, as reported previously. However when other buffer solutions were used on the alkaline side of the minimum, both the lignin and yield curves become discontinuous. In other words, different buffer solutions differ in the severity of their pretreatment effect, even at the same pH. Obviously some other factor besides the hydrogen ion concentration must be considered. Table 14 shows that the salt concentration of the buffer solutions varies somewhat, and it would seem that either this factor or the specific action of some ions other than the hydrogen ion might be involved. That no discontinuity occurs between the two buffers at pH 2 and pH 3 may be explained by the dominating effect of the hydrogen ion in this region. Only when the hydrogen ion concentration is low (on the alkaline side of the minimum) do other factors become noticeable.

Fig. 12 also shows that the sulphur content of the lignin after cooking, varies with the pH of the pretreating solution in a manner exactly opposite to the variation in the residual lignin content of the pulp. That is, when wood is pretreated at about pH 5, the degree of sulphonation of the residual lignin is a maximum, and the lignin remaining as percent of the original wood is a minimum. In other words, the sulphur as percent of pulp after the same length of cook is almost independent of the pH of pretreatment.

7. The Effect of the pH of Pretreatment on the Subsequent Delignification of Spruce Wood in Alkali Liquor

It was desired to determine whether the pretreatment of wood in aqueous solutions hindered alkali cooking in the same manner as sulphite cooking, in the hope that this might throw some light on the nature of the effect. Since it is not very practical to cook wood-meal by the alkali process, chips were used for this experiment. About 10 grams of spruce chips (20 x 10 x 2 mm.) were weighed into small beakers containing the appropriate buffer solutions, and allowed to stand overnight under vacuum to ensure thorough penetration of the solutions. The chips were then heated in their respective solutions for 6 hours at 140°C. Those pretreated at pH 1 were severely burned and were almost black. Both the pretreated chips, and some untreated chips were then cooked according to the standard procedure used by Larocque (47), viz., 3 hours at 160°C. in 2.00 N sodium hydroxide. In each case the resulting pulp was disintegrated, washed thoroughly and treated in the same manner as the sulphite pulps.

The results are shown in Table 15 and the lignin remaining

TABLE 15

The Effect of pH of Pretreatment on Subsequent Delignification in Alkali Liquor

Wood:- spruce chips, 20 x 10 x 2 mm. Density 0.41, lignin 30.9%.

Pretreatment:- 6 hr., 140°C.

Cooking:- Iron bombs, 3 hr., 160°C.

Liquor:- 2.00 N sodium hydroxide.

pH of pretreating solution	Buffer solution	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of original wood
A. Run No. 32, untreated.					
-	-	48.5	46.3	4.50	2.18
B. Run No. 46, pretreated.					
1	HCl, KCl	31.4	10.8	65.6	20.6
2	" "	40.3	35.7	11.4	4.58
3	McIlvaine citric ac. Na_2HPO_4	39.9	36.4	8.67	3.46
5	"	44.0	41.0	6.74	2.96
7	"	46.6	43.3	7.10	3.31

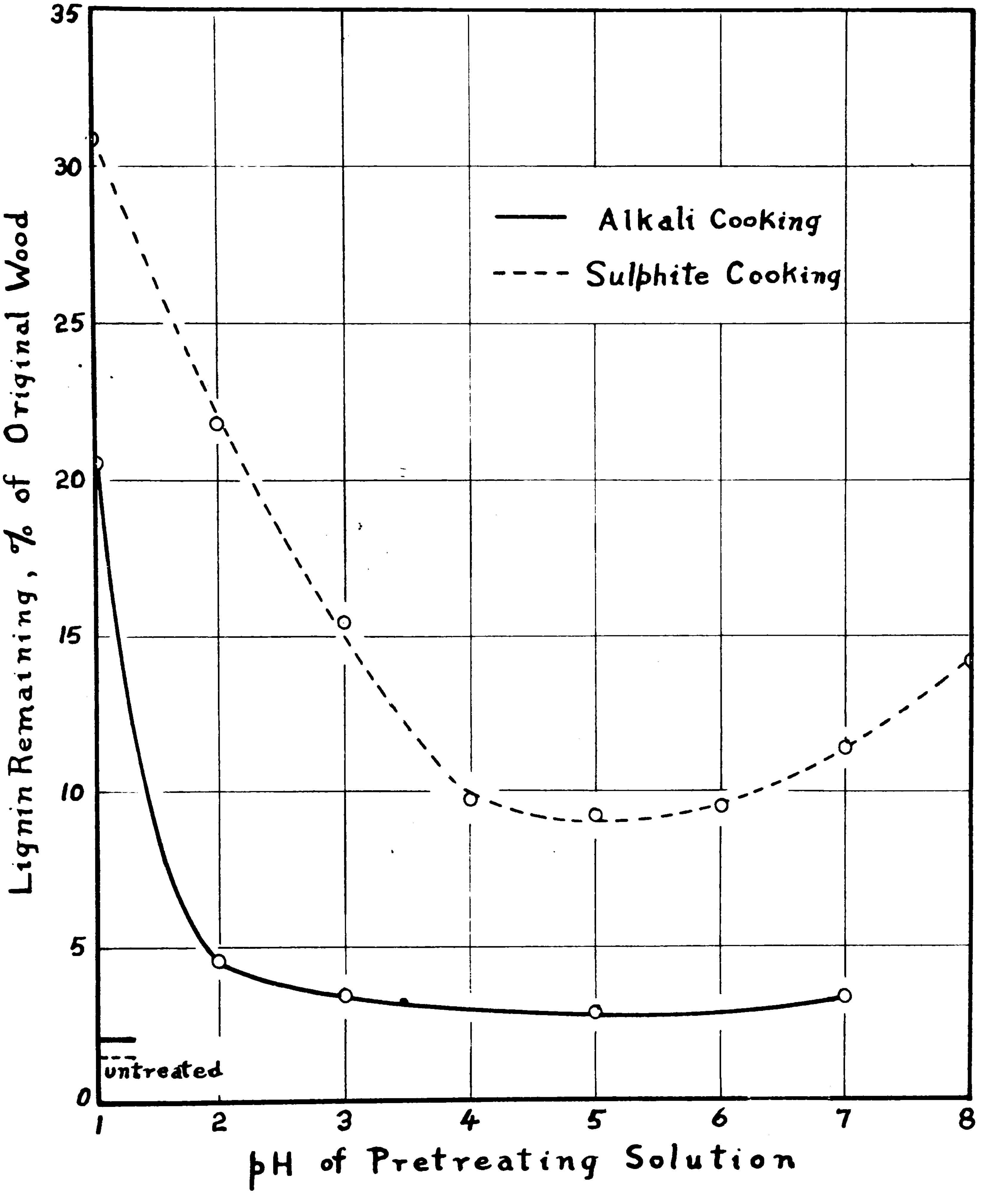


Fig. 13. The effect of pH of pretreatment on subsequent delignification in alkali liquor.

as percent of the original wood is plotted against the pH of the pretreating solution in Fig. 13. The dotted curve is taken from Fig. 12 and serves as a comparison with the sulphite process. It is observed that the pretreated wood was delignified to a much greater extent by the alkali process, even though the untreated wood was delignified less. However, a slight pretreatment effect is noticeable between pH 2 and pH 7, even when cooked by the alkali process, and it is also a minimum at pH 5. The wood pretreated at pH 1 was so severely burned that more cellulose than lignin was removed during cooking in the alkali liquor

B. The Pretreatment of Wood in Neutral Salt Solutions

1. The Effect of Various Anions and Cations in the Pretreating Solution on Subsequent Delignification in Sulphite Liquor

Since different buffer solutions were found to have a different pretreating effect even at the same pH, it was desired to determine the influence of ions other than the hydrogen ion. For the first series, miscellaneous salt solutions were chosen having both mono- and bivalent anions and cations. Samples of wood-meal were pretreated 6 hours at 140°C. in these solutions and in distilled water for comparison. They were then cooked for 3 hours at 140°C. in sulphite liquor. Since the pretreating solutions were not buffered, the pH before and after heating

TABLE 16

The Effect of Pretreatment with Miscellaneous Neutral Salt Solutions on Subsequent Delignification

Run Nos. 34, 36.

Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.

Pretreatment:- 6 hr., 140°C.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Pretreating solution 0.4 equiv. per liter	pH of pretreating solution		Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of original wood
	before	after				
H_2O (dist.)	5.43	4.38	59.2	47.4	19.9	11.8
KCl	5.58	5.01	57.7	46.8	18.9	10.9
NaCl	5.47	4.74	57.9	46.7	19.3	11.2
Na_2SO_4	5.43	4.43	55.9	47.1	15.8	8.8
$NH_4C_2H_3O_2$	6.75	6.09	70.7	48.5	31.3	22.2
$Ca(C_2H_3O_2)_2$	7.48	5.90	63.5	53.2	16.3	10.3

Note:- pH determinations by quinhydrone electrode at room temperature.

was determined at room temperature with a quinhydrone electrode.

The results are shown in Table 16. A small amount of carbon dioxide in the distilled water slightly reduced the pH of the original solutions, and the unavoidable liberation of a small amount of acid from the wood during heating lowered the pH somewhat more. However it is observed that the final pH of the solution in every case was between pH 4 and pH 6, which corresponds to the flat part of the lignin vs. pH curve in Fig. 12. Therefore, variations in the severity of pretreatment reported here cannot be attributed to differences in the hydrogen ion concentration of the different salt solutions.

An inspection of the residual lignin values in Table 16 shows that the effect of potassium chloride in pretreatment is slightly less than that of sodium chloride, and the effect of sodium sulphate is less than that of sodium chloride. This is in the same order as the respective ions in the lyotropic series. It is also observed that ammonium acetate has a very severe pretreatment effect which must be due to the NH_4^+ ion, since it is not observed with calcium acetate. Although these results were not conclusive, they suggested that the effect of neutral salts in pretreatment might be related to the lyotropic series for anions and cations, rather than a discharge effect related to valency.

To test this hypothesis, samples of wood-meal were pretreated in molar solutions of a variety of potassium salts and metallic chlorides, and then cooked in sulphite liquor. The

TABLE 17

The Effect of Anions in the Pretreating Solution on Subsequent Delignification

Run Nos. 35, 37.
Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.
Pretreatment:- 6 hr., 140°C.
Cooking:- Bronze bombs, 3 hr., 140°C.
Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Pretreating solution 1.0 molar	pH of pretreating solution		Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
	before	after						
KCNS	4.77	5.00	68.6	46.6	32.1	22.0	1.47	4.58
KI	7.37	4.47	60.2	46.2	23.3	14.0	1.24	5.32
KBr	5.17	3.91	60.2	48.0	20.2	12.2	1.21	-
KNO_3	4.67	3.94	59.7	47.6	20.2	12.1	1.12	5.54
KCl	5.07	3.84	58.6	47.3	19.2	11.2	1.15	5.98
KH_2PO_4	4.08	4.10	59.7	49.7	16.7	9.95	1.03	6.18
K_2SO_4	4.69	4.15	57.1	48.0	16.0	9.10	0.95	5.91

Note:- pH determinations made by quinhydrone electrode at room temperature.

TABLE 18

The Effect of Cations in the Pretreating Solution on Subsequent Delignification

Run Nos. 37, 39, 42.
Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.
Pretreatment:- 6 hr., 140°C.
Cooking:- Bronze bombs, 3 hr., 140°C.
Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Pretreating solution 1.0 molar	pH of pretreating solution		Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
	before	after						
NH_4NO_3	4.86	3.32	67.2	43.6	35.0	23.6	1.22	3.47
NH_4Cl	4.57	3.90	66.9	44.1	34.1	22.8	1.29	3.79
$SrCl_2$	5.01	3.27	64.4	46.3	28.1	18.1	1.19	4.23
$CaCl_2$	6.57	3.18	63.0	45.7	28.3	17.8	-	-
$BaCl_2$	4.42	3.27	63.5	46.6	26.7	16.9	1.29	4.83
$MgCl_2$	7.7	3.62	61.5	47.3	23.2	14.2	1.21	5.23
LiCl	6.80	3.70	61.3	48.2	21.4	13.1	1.20	5.63
NaCl	4.93	3.74	59.0	47.3	19.8	11.7	1.14	5.77
KCl	5.07	3.84	58.6	47.3	19.2	11.2	1.15	5.98

Note:- pH determinations made by quinhydrone electrode at room temperature.

effect of anions is shown in Table 17 and the effect of cations in Table 18, each arranged in order of decreasing residual lignin content of the pulps. It is observed that the sulphur content of the residual lignin increases as the residual lignin content of the pulp decreases.

The close connection between the observed order of the anions and cations in their pretreating effect and the lyotropic series is apparent at once. Traube (71) has made a detailed study of the lyotropic effect of anions and cations on numerous physico-chemical properties of solutions and lyophile colloids, and gives the series as follows:-

(a) For the hydration of ions:

$CNS < I < Br < NO_3 < Cl < HPO_4 < SO_4$

$NH_4 < K < Na < Li < Ba < Sr < Ca < Mg$

(b) For the swelling of gelatin:

$CNS > I > Br > NO_3 > Cl > SO_4$

A comparison of Table 17 with the above series shows that the order of anions in the severity of their pretreating effect is exactly the reverse of their order in the lyotropic series for the hydration of ions, but is identical with their order in the lyotropic series for the swelling of gelatin. Although molar potassium sulphate exhibits the least pretreating effect of the series, delignification has still been considerably retarded. (Compare untreated wood, Table 12). The potassium sulphate, however, has depressed somewhat the pretreating effect of water alone (Table 16).

The order found for the cations in pretreatment does not agree as well with the lyotropic series. The order of the alkali metal ions in pretreatment is the same as their order for hydrate formation, which is the reverse of that found in the case of the anions. The alkaline earth metal ions all have a greater pretreating effect than the alkali metal ions, as would be expected from the increase in valence. The pretreating effect of NH_4^+ is very severe and entirely out of proportion to its position in the lyotropic series, although ammonium nitrate has a slightly greater effect than ammonium chloride, showing the lyotropic influence of the anion. This severe effect of ammonia was also observed by Corey (15), and appears to be specific.

2. The Effect of Salt Concentration in the Pretreating Solution on Subsequent Delignification

To determine the effect of the concentration of the pretreating solution on subsequent delignification, samples of wood-meal were heated in potassium thiocyanate solutions of zero to 2.0 molar. After pretreatment and washing, the wood-meal was tested for adsorbed thiocyanate, in case it might have some effect on the reaction. A portion of the meal was digested in concentrated nitric acid, and ferric alum indicator added. The test was negative. The pretreated wood-meal was cooked in sulphite liquor as usual. The results are listed in Table 19, and the yield, lignin and sulphur values are plotted

TABLE 19

The Effect of the Salt Concentration in the Pretreating Solution on Subsequent Delignification

Run Nos. 35, 36, 38.

Wood:- spruce meal, 40-100 mesh. Density 0.34, lignin 29.0%.

Pretreatment:- 6 hr., 140°C.

Cooking:- Bronze bombs, 3 hr., 140°C.

Liquor:- 5.1% total, 1.2% combined sulphur dioxide. (Calcium base).

Conc. of KCNS, moles per liter	pH of pretreating solution		Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood	Sulphur, % of pulp	Sulphur, % of lignin
	before	after						
0	5.43	4.38	59.2	47.4	19.9	11.8	-	-
0.05	5.06	5.02	61.5	48.6	21.0	12.9	1.31	6.26
0.10	5.15	4.38	63.4	48.6	23.3	14.8	1.43	6.12
0.40	4.67	4.92	66.0	46.5	29.5	19.5	1.48	5.02
1.00	4.77	5.00	68.6	46.6	32.1	22.0	1.47	4.58
2.00	5.28	5.78	70.4	46.2	34.4	24.2	1.52	4.42

Note:- pH determinations made by quinhydrone electrode at room temperature.

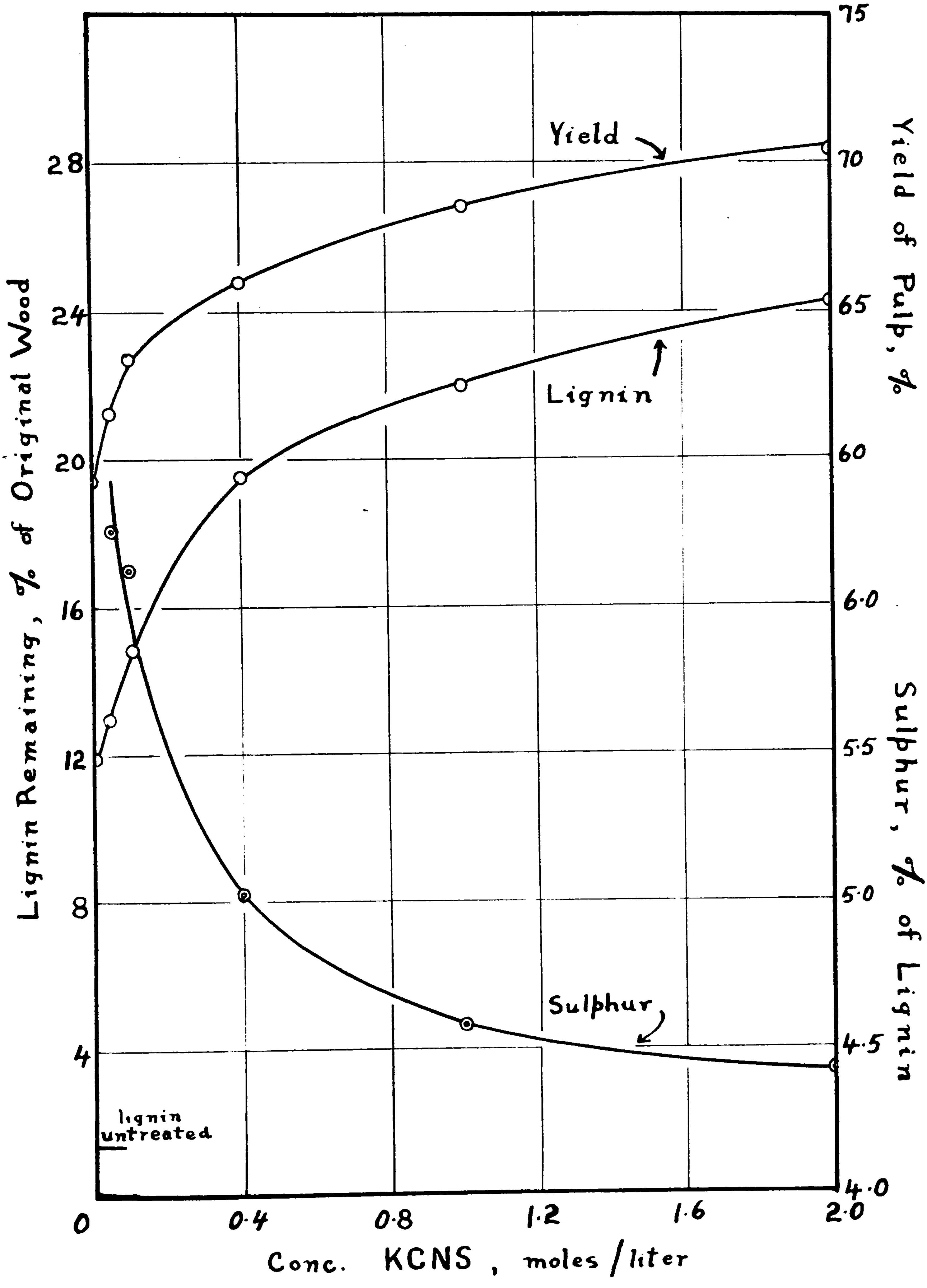


Fig. 14. The effect of concentration of pretreating neutral salt solution on subsequent delignification.

against the concentration of the pretreating solution in Fig. 14.

An inspection of the residual lignin curve shows that the pretreating effect of distilled water alone is quite considerable, and this is increased rapidly at first and then more slowly, by the addition of potassium thiocyanate to the pretreating solution. The sulphur content of the lignin is again inversely proportional to the residual lignin content of the pulp.

SUMMARY OF RESULTS (PART I)

A brief summary of the experimental results is given here to assist in clarifying the discussion which follows.

1. When wood is heated in buffer solutions for a given time at the same pH, the difficulty of subsequent delignification in sulphite liquor increases rapidly with the temperature of pretreatment above 100°C. Below 100°C. the effect of pretreatment is hardly noticeable in 6 hours at pH 3.

2. At the same pH and temperature, the effect of pretreatment increases rapidly at first and then more slowly with increasing time of pretreatment. If pretreatment is carried out for 96 hours at pH 3 and 140°C., no lignin whatever is removed in a sulphite cook which would normally remove 95% of the lignin.

3. The pretreatment of wood for long periods of time at 140°C. converts some of the carbohydrate material into "apparent lignin".

4. The pretreatment of jack pine heartwood in buffer solutions, retards subsequent delignification in sulphite liquor in the same manner as it does spruce wood. The degree of cooking of the two pretreated woods differs only as would be expected from the difference in the cooking properties of the two untreated woods.

5. The rate of delignification of pretreated spruce wood by the sulphite process, is initially much less than that of the untreated wood, but increases with the time of cooking until the two are almost equal.

6. Spruce wood pretreated 36 hours, at pH 3 and 140°C. has been 90% delignified by cooking 21 hours in two stages, indicating that the effect of pretreatment is reversible to a large extent.

7. The pretreatment of spruce wood in buffer solutions for a given time at constant temperature, retards subsequent delignification in sulphite liquor to an extent depending on the pH of the pretreating solution. The effect is a minimum, but nevertheless considerable at pH 5. Above pH 5 the effect of pretreatment varies with the nature and concentration of the buffer salt. Below pH 5 the effect of the hydrogen ion concentration is dominant and the severity of the pretreatment rapidly increases.

8. The pretreatment of spruce wood in buffer solutions, retards subsequent delignification in alkali liquor to a noticeable, but much smaller extent than in sulphite liquor. A slight minimum in the pretreating effect is observed at pH 5 and it becomes severe only below pH 2.

9. The pretreatment of spruce wood in molar neutral salt solutions retards subsequent delignification in sulphite liquor

to an extent depending on the position of the ions of the salt in the lyotropic series.

10. The pretreating effect of distilled water is increased by the addition of potassium thiocyanate, rapidly at first and then more slowly, with increasing salt concentration. Strongly hydrated salts such as the sulphates, somewhat depress the pretreating effect of distilled water.

11. Ammonium salts exert a drastic action in pretreatment, entirely out of proportion to their position in the lyotropic series, rendering subsequent cooking by the sulphite process almost impossible.

DISCUSSION AND CONCLUSION (PART I)

It has been shown, not only in the present work, but by a number of other investigators as well, that lignin is altered in some manner when subjected to treatment in various acids or hot aqueous solutions, which makes it very difficult to dissolve in sulphite liquor. Some claim that a chemical change in the lignin has been brought about, while others maintain that the change is purely physical. Since our present knowledge of the structure of lignin is so limited, it is impossible to more than theorize regarding the exact nature and mechanism of this change. However, the various points of view will now be discussed in the light of the evidence presented here.

Miller and Swanson (52, p.87) subjected spruce wood-meal to a preliminary hydrolysis for 6 hours at 100°C. in 0.005 to 0.5 N hydrochloric acid, followed by cooking in sulphite liquor. They found that delignification was retarded to an extent depending on the severity of the acid pretreatment and concluded that the hydrogen ion concentration was the controlling factor. These authors believed that some chemical change in the lignin occurred which blocked the point where the bisulphite normally adds, thus retarding the reaction. In addition, they suggest that the phenomenon is identical with burning in a sulphite cook.

Hägglund (33) isolated lignin from spruce wood by various types of treatment in concentrated hydrochloric acid. He observed that the solubility of the product in bisulphite solutions at 135°C. was much less than that of natural lignin, and decreased with increase in the severity of the acid treatment used in its preparation. Hägglund suggested that lignin so prepared existed in greater molecular complexes than natural lignin, but was unable to say whether a polymerization or a condensation had occurred. He likened the change to that in which certain sugars in high concentration, when treated with hydrochloric acid, combine to form polymeric carbohydrates, which through heating in dilute acids are again split into simple sugars. However it has been shown in the present work that heating wood in dilute acids produces similar effects to more concentrated acids at lower temperatures, so that Hägglund's explanation of the reversibility of the phenomenon is not valid.

Freudenberg (22) treated wood in 5% sodium hydroxide for 24 hours followed by 1% sulphuric acid for 4 hours, both at room temperature. The wood was then subjected to a normal sulphite cook. The rate of delignification was so retarded that Freudenberg concluded that no change in the particle size or surface area of the lignin could account for the difference, and that therefore a chemical change in the lignin must have occurred. If we assume spherical particles, it can be shown that a thousandfold change in particle size would be required to cause a tenfold change in surface area.

Corey (15) points out that, if pretreatment causes a chemical polymerization or condensation of the lignin which blocks the group to which the bisulphite adds, then the process must be reversible, since pretreated wood can be delignified if cooked for a sufficient length of time. If the polymerization or condensation is caused by heating in aqueous solutions it is difficult to understand how the process can be reversed by heating in sulphite liquor. On the other hand, if the agglomeration is purely physical, the cooking reaction would take place as usual except for a decrease in velocity in proportion to the decrease in exposed surface area of the lignin.

Corey and Maass (16, 17, 18) have therefore favoured the hypothesis that the pretreatment of wood in aqueous solutions causes a physical agglomeration of the lignin particles to form larger aggregates. They suggest that the delignification of both untreated and pretreated wood by the sulphite process is purely a surface reaction, the rate of which is governed only by the exposed surface area of the lignin particles, other conditions being constant. Hence any decrease in surface area caused by an agglomeration of the lignin, would decrease the rate of cooking. This line of reasoning explains many of the observed phenomena, but it is not altogether satisfactory

The Rate of Delignification of Untreated Spruce Wood

The kinetics of the delignification of untreated spruce wood by the sulphite process will be dealt with more fully in Part II. However, it is necessary to consider the subject briefly here before discussing further the phenomena of pretreatment. Although Corey and Maass (18) reported systematic deviations of the reaction from the first order relationship, no attempt was made to interpret them. As mentioned previously, these authors suggested that the delignification of untreated wood was approximately first order due to the cancellation of two opposing effects, viz., a tendency of the lignin to agglomerate into larger particles due to the acidity of the liquor, and a simultaneous decrease in size due to the cooking action.

However, it has never been demonstrated that the retarding action observed in pretreatment is actually present in a normal sulphite cook of untreated wood. Since sulphite liquor differs from all other aqueous solutions in its effect on lignin, one is not altogether justified in assuming that the same retarding action occurs in both. In any case the cooking action is more rapid than the pretreatment effect and we will neglect the latter for the time being. It will now be shown that better agreement between the particle size theory of Corey and Maass and experiment is obtained, if we abandon the conception that the reaction is approximately first order due to the fortuitous cancellation of two opposing tendencies.

Let us assume for the moment that lignin does exist in wood in the form of submicroscopic particles, and that the rate of delignification is determined by the exposed surface area of the lignin, other conditions being constant. We shall suppose that only the surface of the lignin is accessible to the cooking reagent; that the lignin particles are approximately spherical in shape and decrease in size in a uniform manner as cooking proceeds; and that diffusion processes are more rapid than chemical reaction so that a constant concentration of reagent at the surface is maintained.

From elementary mensuration formulae it can readily be shown that the surface area of a sphere is proportional to the two thirds power of its volume, and since the quantity of lignin present is proportional to the total volume of the particles, the rate of lignin removal will be given by the equation:

$$- \frac{dL}{dt} = k\, L^{2/3} \quad \ldots\ldots\ldots\ldots \quad (3)$$

On integration this becomes:

$$k = \frac{3}{t} \left[L_o^{1/3} - L^{1/3} \right] \quad \ldots\ldots\ldots\ldots \quad (4)$$

where k = the velocity constant,

L_o = the initial lignin content, and

L = the lignin content at time "t", both expressed as percent of the original wood.

Now, if our assumptions are correct, it is obvious that a straight line will be obtained when "$L^{1/3}$" is plotted against the time of cooking. This has been done by recalculating the data for the rate of delignification of untreated wood from Table 12, and the result is shown in Fig. 15, A. It is observed that the experimental points fall closely on a straight line until 95% of the reaction has been completed. The same data are plotted for comparison in Fig. 15, B, according to the first order relationship (log L vs. time). In this case a reversed S-shape curve is obtained, which departs considerably from the straight (dotted) line. It is this deviation from the unimolecular law for which the particle size theory offers an explanation, since Equation (4) fits the experimental data better than Equation (2).

Although we are not greatly interested in the final stages of the reaction, the falling off in rate at the end of the cook (Fig. 15, A) may readily be explained. It may be due to a small, but consistent error in the lignin determination which only becomes apparent when the quantity of lignin is small. On the other hand, it is possible that a small amount of lignin is enclosed in the cell wall in such a manner that it cannot be removed, even though the reagents are able to diffuse in and attack it. Larocque (47) has observed a similar falling off in rate in the final stages of alkali cooking, which he attributes to a small amount of more resistant lignin. Additional evidence in support of Equation (4) will be presented in Part II.

The assumption of spherical particles of lignin may well be questioned. However, the shape of the particles might vary considerably without causing much departure from the above

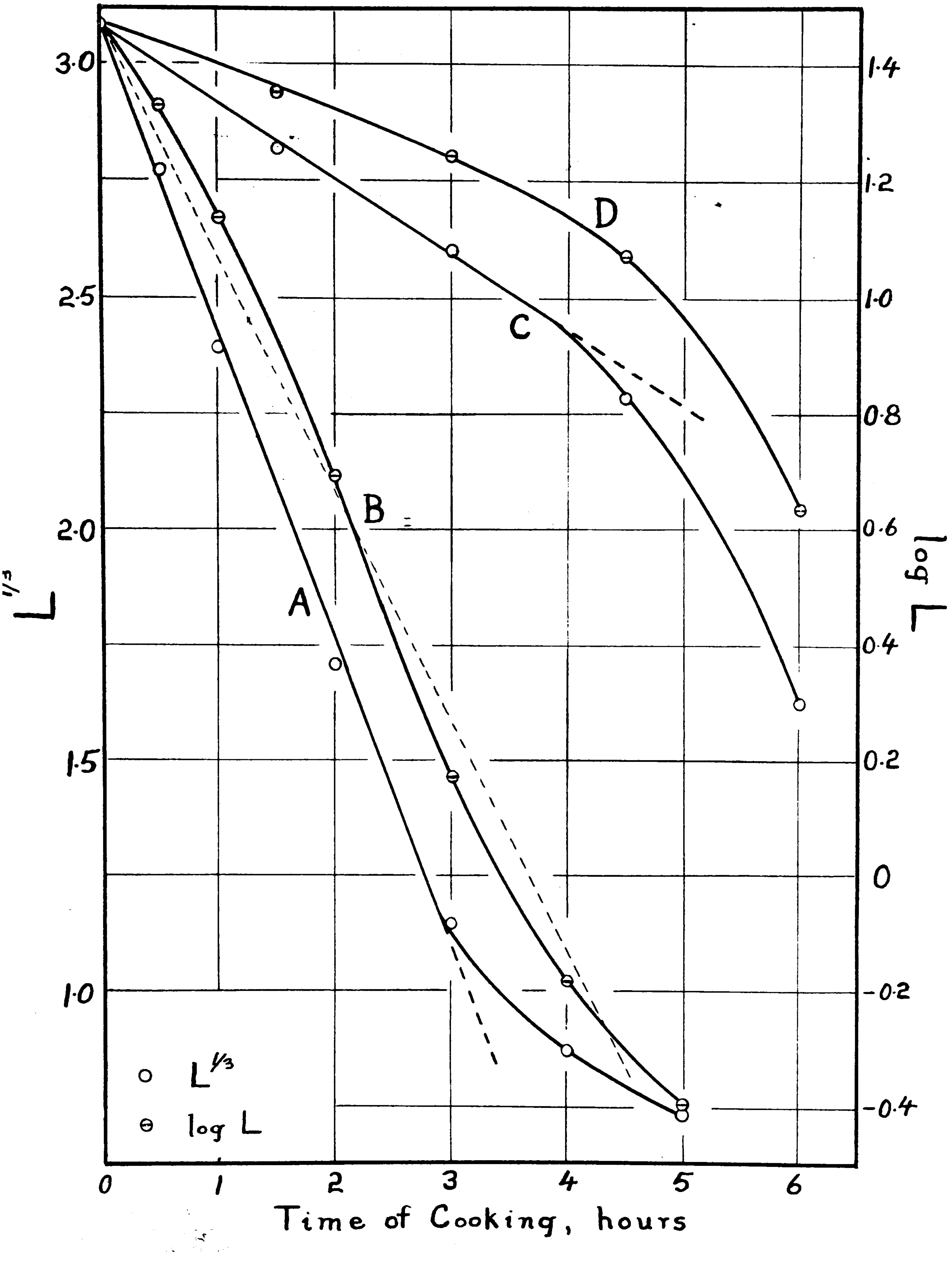


Fig. 15. The rate of delignification of untreated and pretreated spruce wood. A and B, untreated; C and D, pretreated 36 hr., pH 3, 140°C. (time scale x 2)

relationship, provided erosion were not too irregular. The assumption of diffusion processes more rapid than chemical reaction is justified from the evidence of the temperature coefficient presented in Part II. That only the surface of the lignin should be accessible to the reagents, is a more debatable point. It has been suggested that lignin may resemble a gel somewhat in structure because of its colloidal properties. If this is true, one would expect the relatively small hydrogen and bisulphite ions to diffuse into any part of it.

Yorston (78) has provided considerable evidence to show that all parts of the lignin are accessible to the reagent. The sulphur content of the lignin found in various stages of sulphite cooking, would indicate an impossibly high concentration of sulphur if sulphonation were limited to the surface of the lignin particles. In addition, an appreciable amount of sulphur is found in the residual lignin after partially cooked wood is hydrolysed to a low lignin value in buffer solutions. This sulphur must therefore have penetrated to the least accessible portions of the lignin. However, sulphonation is not uniform throughout the lignin since the ratio of sulphur to lignin decreases during the hydrolysis in buffer solutions, the more highly sulphonated lignin being removed first.

The present work substantiates that of Yorston. Fig. 11 shows that the average sulphur content of the residual lignin increases in a linear manner with the time of cooking for untreated wood. However, if the sulphonation were restricted to the surface layer of the lignin particles, the ratio of sulphur to lignin would increase in an exponential manner as cooking proceeds and the particles become smaller. This does not necessarily invalidate the particle size hypothesis, since the rate of sulphonation may perhaps be greater than the rate of removal of sulphonated lignin, and the latter may still be determined by the area of the exposed surface. On the whole, the evidence presented does support the hypothesis that the rate of delignification of wood by the sulphite process might be governed by the particle size of the lignin, other conditions being constant.

The Rate of Delignification of Pretreated Spruce Wood

The fact that the rate of delignification of pretreated wood increases during cooking can be explained in a qualitative manner on the basis of Corey and Maass' hypothesis. If pretreatment causes a physical agglomeration of lignin particles, the exposed surface area of which determines the rate of subsequent cooking, then obviously, the rate will be initially much less than that of untreated wood, but will approach the latter as the lignin particles are reduced to their original size by the cooking action. However, if this hypothesis is correct, we would expect a plot of "$L^{1/3}$" against the time of cooking to give a straight line, as in the case of untreated wood, differing only in slope in proportion to the difference in particle size.

In Fig. 15, C, the data from Table 13 for the first stage of cooking of the wood pretreated 36 hours, pH 3, 140°C. is plotted according to the relationship, "$L^{1/3}$ vs. time." The same data is shown in Fig. 15, D, plotted for comparison according to the first order relation (log L vs. time). It is observed that neither relation gives a straight line, except for the first half of the reaction. From the shape of the curve, Fig. 15, C, we see that after about half of the lignin has been removed, the rate of reaction increases to a much greater extent than the particle size hypothesis would predict. This could be explained if the erosion were irregular, since the effective surface area would increase much more rapidly in proportion, than if the lignin were removed uniformly. This departure from the theory was not observed in the case of untreated wood (Fig. 15, A). The only other explanations are that the agglomerated particles suddenly split up into their original units, or else that some chemical change is involved in pretreatment.

It is of interest to calculate the difference in particle size which would produce the observed difference in the rates of delignification of the untreated and pretreated woods, on the basis of Corey and Maass' hypothesis. Let

$n =$ the number of lignin particles per gram of wood,
$r =$ the radius of a particle,
$S =$ the total surface area of "n" particles.

The subscript

1 refers to the untreated wood, and

2 refers to the pretreated wood.

Now, the ratio of the total surface areas in the two cases is given by the equation:

$$\frac{S_1}{S_2} = \frac{n_1 r_1^2}{n_2 r_2^2} \quad \ldots\ldots\ldots\ \ldots\ldots \quad (5)$$

and since the total volume of the particles remains unaltered,

$$n_1 r_1^3 = n_2 r_2^3 \quad \ldots\ \ldots\ldots\ldots\ldots \quad (6)$$

Eliminating "r_1" and "r_2" from Equations (5) and (6), we obtain:

$$\frac{S_1}{S_2} = \left[\frac{n_1}{n_2}\right]^{1/3} \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

From the straight line portions of the curves A and C (Fig. 15), the velocity constants for the delignification of the untreated and pretreated woods were calculated according to Equation (4):

	k
(a) The untreated wood	1.97
(b) The pretreated wood	0.242

By substituting these values of "k" in Equation (3), the actual rates of delignification of the untreated and pretreated woods at any instant during the first half of the reaction are obtained:

$$\text{(a)} \qquad -\frac{dL}{dt} = 1.97\ L^{2/3}$$

$$\text{(b)} \qquad -\frac{dL}{dt} = 0.242\ L^{2/3}$$

Now, since the rate of delignification in each case is assumed proportional to the total surface area, and the comparison is made at equal lignin contents, then

$$\frac{S_1}{S_2} = \frac{1.97}{0.242}$$

Substituting in Equation (7) and solving, we obtain:

$$\frac{n_1}{n_2} = \left[\frac{1.97}{0.242}\right]^3 = 540$$

That is, on the basis of Corey and Maass' hypothesis, an increase in the particle size of the lignin of approximately 500 times would be required to account for the observed difference in the rates of delignification of the untreated and pretreated woods. This is rather a large amount. Since it is easier to imagine a coagulated particle as a cluster of small particles rather than a uniform sphere, an even greater change in size would be required to produce a sufficient difference in the total surface area. It therefore seems probable that some other change also occurs during pretreatment.

An interpretation of the values for the sulphur content of the residual lignin for the untreated and pretreated woods at various stages in the cooking process is difficult to make. This is due to the fact that we do not know the sulphur content of the lignin which has been removed. A smaller sulphur content of the lignin remaining may be due either to a decrease in the rate of sulphonation of the lignin, or a decrease in the rate of removal of sulphonated lignin. If we make the comparison at equal times of cooking as in Fig. 11, the sulphur content of the lignin in the untreated wood is much greater, but the lignin content of the pulp is also much smaller. On the other hand, if we make the comparison at equal residual lignin values as recommended by Yorston (75), the sulphur content of the lignin in the pretreated wood is greater, but the cooking has been carried out about six times as long. Consequently, we cannot say to what extent the sulphonation reaction has been retarded by the pretreatment.

Compare now, the rates of delignification of untreated and pretreated woods containing lignin sulphonated to the same extent. Tables 12 and 13 show that the untreated wood cooked one hour and the pretreated wood cooked six hours, both contain 4.81% sulphur in the lignin. However, the slopes of the lignin curves in Figs. 10 and 15 show that at these points the rate of delignification of the untreated wood is about 8 or 9 times greater than that of the pretreated wood. Although all of the sulphur may not be taken up in a form which assists delignification, it is quite evident that the second reaction, whether it be an hydrolysis or not, is definitely retarded by the pretreatment, and to a greater extent than the sulphonation reaction.

With regard to the second stage of the delignification of the pretreated wood, no explanation can be offered for the observed discontinuities without further investigation.

Other Pretreatment Phenomena

It is quite reasonable that the severity of the pretreating effect should be increased by an increase in both the temperature and the time of treatment, no matter what the nature of the phenomenon or the mechanism by which it is brought about.

The formation of apparent lignin requires further comment. It was pointed out in the analytical section that when wood is treated with sulphuric acid for the determination of lignin, too high a value will be obtained if the acid is allowed to get hot or the treatment continued too long. Hawley and Harris (36) found that when Cross and Bevan cellulose was heated at 135°C. for several days, large amounts of lignin-like substances were formed, apparently from hexosans in the wood. This product was designated "synthetic lignin", because it displayed many of the chemical properties of natural lignin. Since insolubility in the lignin determination is partly due to molecular size, it was concluded that a polymerization of the hexosan had occurred. It is believed that the formation of apparent lignin during pretreatment is also due to a polymerization of some of the hemicelluloses present in wood.

It has been shown that the pretreatment of wood in buffer solutions between pH 2 and pH 7, only very slightly retards subsequent delignification in alkali liquor as compared with sulphite liquor. This may be due to the fact that all of the pretreated lignin is more readily accessible to alkali liquor than to sulphite liquor. On the other hand, it is possible that pretreatment does cause some chemical change in lignin which retards the sulphonation reaction, as claimed by Miller and Swanson (52). This would not necessarily affect subsequent alkali cooking.

The severe pretreating effect observed with all ammonium salts is similar to that reported by Corey (15) and by Benson et al (5). These latter workers pretreated Douglas fir chips in 5 percent ammonia at 70°C. to remove resins. They found that if the temperature exceeded 70°C. or if the pretreatment were continued too long, the chips could not be satisfactorily cooked in sulphite liquor. Since heating in water at 102°C. for 3 hours produced no appreciable effect on subsequent cooking, they concluded that ammonia exerted a specific chemical action on the lignin. The present work substantiates this conclusion.

It has been shown that the effect produced on subsequent delignification, by heating wood in neutral salt solutions, depends on the position of the ions of the salt in the lyotropic series. Whether pretreatment causes only an agglomeration of lignin into larger particles, or whether it causes some chemical change, it is equally difficult to understand why the addition of neutral salts would increase the pretreating effect of water alone.

Stamm (64, 65) has shown that saturated solutions of chlorides and potassium salts cause a swelling of wood at room temperature, beyond the normal water swollen state, in the following order:

$$CNS > I > CrO_4 > Br > Cl > NO_3 > SO_4 > CO_3$$

$$Zn > Li > Ca > Mg > Mn > Ba > Na > NH_4 > K$$

Decrease in the salt concentration decreases the extent of swelling. According to Herzog and Beck (38), saturated solutions cause a peptization or partial dispersion of cellulose at temperatures above 135°C., in the order:

$$CNS > I > Br > NO_3 > SO_4$$

$$Ca > Ba > Li > Na > K > NH_4$$

The similarity between the order of the ions in their effect on swelling, peptization and pretreatment is apparent, but if any connection exists it is obscure. Whether some cellulose could be partially dispersed during pretreatment and then reprecipitated on the lignin in some manner so that subsequent cooking would be retarded, is impossible to state; whether swelling could play some part in the phenomenon or not, is equally uncertain.

The pronounced minimum in the pretreatment effect at pH 5, also reported by Corey and Maass (17), has never been explained.

Stamm (63) has found that pH has no effect on the external swelling of wood, below pH 11. On the other hand, lyophile colloids such as gelatin, which undergo an increased swelling on the addition of solutions of neutral salts in the order of the lyotropic series, also exhibit a marked minimum in swelling and other physical properties at pH 4.7 (the iso-electric point). This makes the minimum in the pretreatment effect, observed at about pH 5, rather suggestive. However it is impossible to more than conjecture on these points at the present time.

Corey (15) maintains that when wood is heated in aqueous solutions the change which occurs in the lignin is not caused by any specific action of water itself, as claimed by Aronovsky and Gortner (1), but is due to the presence of other ions. In the case of pretreatment in distilled water, Corey suggests that the action is due to acetic acid liberated from the wood, and that the hydrogen ion concentration at the lignin surface might be greater than in the body of the solution. However, the pH could hardly be less than 4 because of the small concentration of acetic acid (a weak acid) and the rapid diffusion of the hydrogen ion; and we have seen that between pH 4 and pH 6, the hydrogen ion concentration has very little effect on pretreatment. When wood is pretreated in buffer solutions at pH 5, the retarding effect on delignification, although a minimum, is still relatively great, and cannot be accounted for by the small concentration of citrate and phosphate ions. In addition, it has been shown that the pretreating effect of distilled water is depressed by the addition of neutral sulphates, i.e., salts which are strongly hydrated and which therefore reduce the effective concentration of water molecules. The only explanation is, that water itself is responsible for part of the pretreatment effect.

Conclusion

It has been shown that the hypothesis advanced by Corey and Maass (16, 17), that the pretreatment of wood in aqueous solutions causes a physical agglomeration of the lignin into larger particles, explains only a portion of the phenomena in a qualitative manner. That the rate of delignification might be proportional to the particle size and exposed surface area of the lignin, gains more support from the experimental data for the cooking of untreated wood than it does from the cooking of pretreated wood.

Since pretreatment can be continued to an almost unlimited degree of severity, visible from a slight brown colouration of the wood to a complete blackening, the writer believes it impossible that no more than a physical change could be involved. The specific action of ammonia, coupled with the reactive nature of lignin, leads us to the conclusion that some chemical change, which may be in some degree reversible, also takes place. The chief argument advanced by Corey (15) against a chemical change in lignin caused by heating wood in aqueous solutions is that it is difficult to explain its apparent reversibility. However, it is not impossible that pretreated lignin can be broken down in some manner by the cooking action, and removed from the wood (at a decreased velocity) without returning to its original state.

When wood is heated in water, some retarding effect on subsequent sulphite cooking appears to be caused by the water alone, and this effect is either increased or decreased by the addition of various ions to the pretreating solution. If it were possible to measure the velocity of this retarding action, and determine its temperature coefficient independent of the opposing cooking reaction, we would be better able to theorize regarding the nature of the phenomenon. Corey was unable to detect any retarding action in the normal sulphite process when the cooking of untreated wood was commenced at 120° and completed at 140°C. He concluded that the temperature coefficients of the pretreatment effect and the cooking reaction were approximately the same. Since the temperature coefficient of delignification is that of a chemical reaction (about 2.0 per 10°C.), this might be construed as additional evidence that pretreatment also causes a chemical change. On the other hand, the retarding effect of pretreatment may not be present in sulphite liquor at all.

No further evidence has been obtained, as to whether the effect of pretreating wood in aqueous solutions is identical with burning in a sulphite cook, as claimed by Miller and

Swanson (52). Certainly, both effects have many characteristics in common. Corey (15) claims that, while pretreatment causes an agglomeration of unsulphonated lignin which is reversible, burning in a sulphite cook results from a polymerization of sulphonated lignin which is not reversible. However, his evidence is not conclusive. In either case, the study of the pretreatment phenomena is important from the practical, as well as the theoretical point of view. It has shown the disadvantage of a high salt concentration in sulphite liquor, and the danger of various types of pretreatment which have been tried commercially to improve penetration or cooking.

From the evidence presented, it is believed that heating wood in aqueous solutions may bring about both physical and chemical changes in the lignin which render subsequent cooking by the sulphite process more difficult. It is clear, that an intimate study of the colloidal properties of lignin will be required to further elucidate some of the phenomena. The rate of delignification of wood pretreated in various ways and at different temperatures should be investigated more fully. In view of the severe action of ammonia in pretreatment, a study of the rate of delignification of untreated wood in ammonium base sulphite liquor, as compared with calcium or sodium base liquor might prove interesting.

PART II

The Rate of Delignification of Untreated Spruce Wood in Sulphite Liquor

PART II

The Rate of Delignification of Untreated Spruce Wood in Sulphite Liquor

INTRODUCTION

When studying the kinetics of any chemical reaction, it is customary to measure reaction velocities at different temperatures and to vary the initial concentration of each reactant over as wide a range as possible. From the information so obtained it is frequently possible to elucidate the probable mechanism of the reaction. In the case of the delignification of wood in sulphite liquor, the problem is complicated by the large number of variable factors involved and by the fact that the reaction is heterogeneous. Nevertheless, a thorough investigation of the influence of liquor composition and temperature on the reaction velocity, under such conditions that undesirable factors could be eliminated and without the restriction imposed by commercial practise, was felt to be essential. In addition to the theoretical significance of such a fundamental investigation, the practical importance to the sulphite industry of an accurate knowledge of the effect of each variable studied is obvious.

Due to the fact that the effective liquor concentration in commercial cooks depends more on digester operation than on the initial composition of acid, the question of liquor concentration is one of the most controversial in the sulphite industry (35). None of the factors, temperature, pressure, or composition can be maintained constant, and it is therefore impossible to determine the actual relation of liquor concentration to the course of the cooking under mill conditions. It is generally believed that an increase in free sulphur dioxide increases the rate of pulping, but that the combined sulphur dioxide, in excess of a certain minimum, is of little consequence. Up to the present time, no quantitative relations have been established.

Stangeland (66) made a few laboratory cooks with different total sulphur dioxide concentrations, but his results are not reliable because he used low liquor ratios, measured the removal of all "incrustants" rather than lignin, and did not vary the combined sulphur dioxide. De Montigny and Maass (19) reported a few experiments on the effect of varying the liquor concentration on the rate of delignification. However the experimental conditions used were such that their results are only of a qualitative nature. McGovern (50) made a series of semi-commercial cooks with liquor containing initially 1.2% combined, and 5 to 20% total, sulphur dioxide. He showed that the rate of cooking increased with the strength of the acid, but to a decreasing extent at the higher concentrations.

Miller and Swanson (52) maintain that the "excess" sulphur dioxide (total -2x combined) governs the rate of cooking. Gishler and Maass (23), on the other hand, have shown from a study of the equilibria existing in calcium base sulphite liquor, that a complex ion corresponding to 2CaO to $3SO_2$ might exist, in which case the true free sulphur dioxide would correspond to the total -1.5 x combined. Mitchell and Yorston (53) obtained some evidence in support of this view by cooking resin extracted sawdust in various sulphite liquors. However, insufficient data were obtained to make the results conclusive.

In the present work, the rate of delignification of resin extracted spruce wood was first investigated in calcium base sulphite liquor. The initial liquor composition was varied over as wide a range as possible, but due to the solubility restrictions in this system, the effect of a high combined sulphur dioxide could not be determined. Magnesia base sulphite liquor was then used, because the greater solubility of magnesium sulphite and bisulphite permitted a more complete investigation of the composition variables. In addition a study of the cooking of spruce wood in magnesium, as compared with calcium, base sulphite liquor was of great practical interest, since a number of advantages have been claimed for the former in the literature (7, 10).

With regard to the variation in reaction rate with temperature, very little quantitative information is available, because it is impossible to cook chips at constant temperature without burning. The use of wood-meal overcomes this difficulty The results of Stangeland (66) and Corey and Maass (18) already referred to, indicate that the temperature coefficient of the reaction is approximately 2.0 per 10°C. between 110° and 140°C.

It was desired to repeat the latter work more accurately and over a greater temperature range. Particular interest lay in low temperature cooks for several reasons. It has been a common belief in the industry that wood cannot be satisfactorily delignified below 110°C., and Sankey and Hibbert (58A) have claimed that the sulphonation reaction does not take place below this temperature. If this were true, a change in the slope of the temperature coefficient curve would be expected, and this might give another clue to the mechanism of the reaction. A quantitative study of the effect of temperature on the yield of pulp was of both theoretical and practical interest.

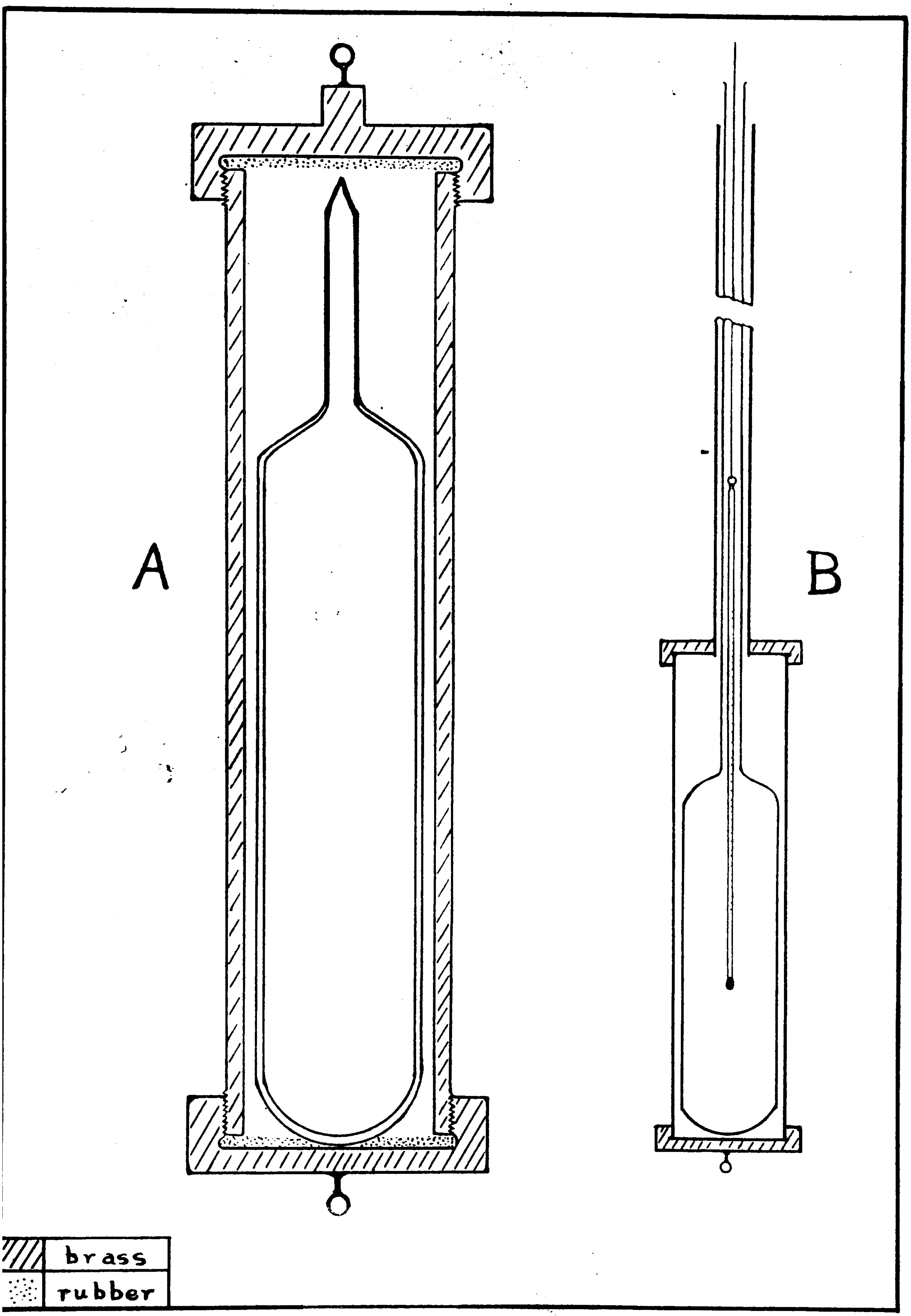
EXPERIMENTAL

The wood used in all of the experiments described in Part II, was well-seasoned white spruce of density 0.43, all cut from the same log. It was ground and sieved to 40 to 100 mesh, and extracted with alcohol-benzene (1:2) for 12 hours in a Soxhlet apparatus.

Several preliminary cooks were made in the 200 cc. bronze bomb digesters used in Part I. It was found that the rubber gaskets used in sealing the bombs were attacked by the liquor at cooking temperatures, resulting in some loss of sulphur dioxide. Since all the cooks described in Part I were made at the same liquor concentration, the results reported are still comparable. However, when it was desired to determine the effect of varying the liquor composition, it was necessary to devise a method by which the liquor concentration could be accurately known and controlled.

Pyrex bombs of 100 cc. capacity were constructed, 1 3/8 inches in diameter and 5 inches long, with a neck 3/8 by 3 inches (Fig. 16, A). Six bombs were used for each run, and 2 grams of the prepared wood-meal of known moisture content were weighed into each bomb. Sulphite liquor of the desired concentration was cooled below 0°C. to minimize loss of sulphur dioxide, and poured into the bombs leaving just sufficient space to permit expansion of the liquid at 130°C. The liquor was then cooled further, the air was flushed out by a stream of sulphur dioxide gas, and the tips of the bombs were sealed off. The bombs were usually allowed to stand at room temperature over night ensuring thorough penetration of the liquor into the wood-meal. Under these conditions the liquor ratio was about 50:1, ten times that used in commercial practise. This minimized the variation in concentration during cooking due to the consumption of lime and sulphur dioxide.

For cooks above 100°C., each glass bomb was provided with a metal casing capable of withstanding high pressures (Fig. 16, A). The space between the bomb and the jacket was filled with water to reduce the pressure difference and improve the heat conduction. The six bombs and casings were dropped into the large thermostat at the desired temperature, which was maintained constant throughout the cook. For temperatures below 100°C., the small thermostat was used and the glass bombs were placed directly in the bath, without the protective casings.



J.M.C. 14/3/38.

Fig. 16. The 100 cc. pyrex bomb digester with protective brass casing. A, for cooking; B, for determining the rate of heating.

In either case, the bombs were allowed to rest on their sides to prevent accumulation of the wood-meal at one end. At suitable intervals the bombs were removed and quenched in water.

After the bombs were cooled below 0°C., they were opened, and the liquor was analyzed immediately. Analysis after cooking was necessary because some sulphur dioxide is always lost when filling the bombs and a small decrease in concentration occurs during cooking, in spite of the high liquor ratio. Therefore, the mean liquor concentration was taken as the average of that for all the bombs in a given run, as determined after cooking. The cooked wood-meal was filtered, washed with tap water, oven dried, weighed and analyzed for lignin by the Ross-Potter method. All yields were calculated on the resin extracted, bone-dry wood basis.

Correction for the Sulphur Dioxide in the Vapor Phase

When the bombs are heated to the cooking temperature, some sulphur dioxide passes into the vapor phase, the amount depending on the volume of the phase and the partial pressure of the gas at the particular temperature. This reduces slightly the concentration of the liquid, and necessitates a correction. From a calibration of the bombs, the volume of both liquid and vapor phases at the cooking temperature could be calculated, allowing for the cubical expansion of the liquid. The latter was taken to be the same as that of water since the correction in any case is small.

The weight of sulphur dioxide in the vapor phase is given by the following equation:

$$\frac{64\ V}{22400} \times \frac{273}{T} \times \frac{P}{76} \quad \text{(grams)} \quad \ldots\ldots\ \ldots \quad (8)$$

where V = the volume of the vapor phase at T°K., in cc.

P = the partial pressure of SO_2 at T°K., in cm. Hg.

The partial pressure of the gas for the desired concentration and temperature was obtained by extrapolating the data of Gurd, Gishler and Maass (27), and Beazley (3). The weight of sulphur dioxide in the vapor, calculated in this manner, was subtracted from the weight in solution as determined by analysis to give the correct concentration. For cooks below 90°C., this correction was negligible.

Correction for the Rate of Heating of the Bombs

The observed time of cooking was taken from the moment the bombs were dropped into the hot bath to the moment they were quenched in water. It was apparent, however, that the time required for the bombs to reach the cooking temperature would introduce an appreciable error in the results. Previous investigators have made various rough estimates to correct for this error in timing, or have ignored it completely.

Since most of the cooking experiments were carried out at 130°C., the determination of the time correction for this temperature will be described in detail. Sensitive pressure gauges were not available, so that an indirect method was used to determine the heating curve accurately. One glass bomb and casing were fitted with stems (as shown in Fig. 16, B), so that a thermometer could be suspended in the centre, while both were immersed in the oil bath. Heating curves were then obtained for the following:

(a) Bomb and casing filled with water at 20°C.; bath at 100°C. (Fig. 17, A).

(b) Bomb and casing filled with oil at 20°C.; bath at 100°C. (Fig. 17, B).

(c) Bomb and casing filled with oil at 20°C.; bath at 130°C. (Fig. 17, C).

The rate of heating of the oil differs from that of the water because of the difference in heat capacity and heat conductivity of the two liquids. However, with the thermostat at 100°C. the ratio of the times to a given temperature for (a) and (b) was approximately constant. Hence from (c) the desired heating curve could be calculated:

(d) Bomb and casing filled with water at 20°C.; bath at 130°C. (Fig. 17, D).

This was considered sufficiently close to the actual conditions of a cook with sulphite liquor.

The calculated curve (d) is exponential, the temperature of the bomb rising rapidly at first, but more slowly as the temperature of the bath is approached. It was therefore necessary to determine the amount of cooking which took place during the heating period.

Assuming a temperature coefficient of the sulphite process of 2.0 per 10°C., and a linear change in temperature, Yorston (76) derived the following relation:

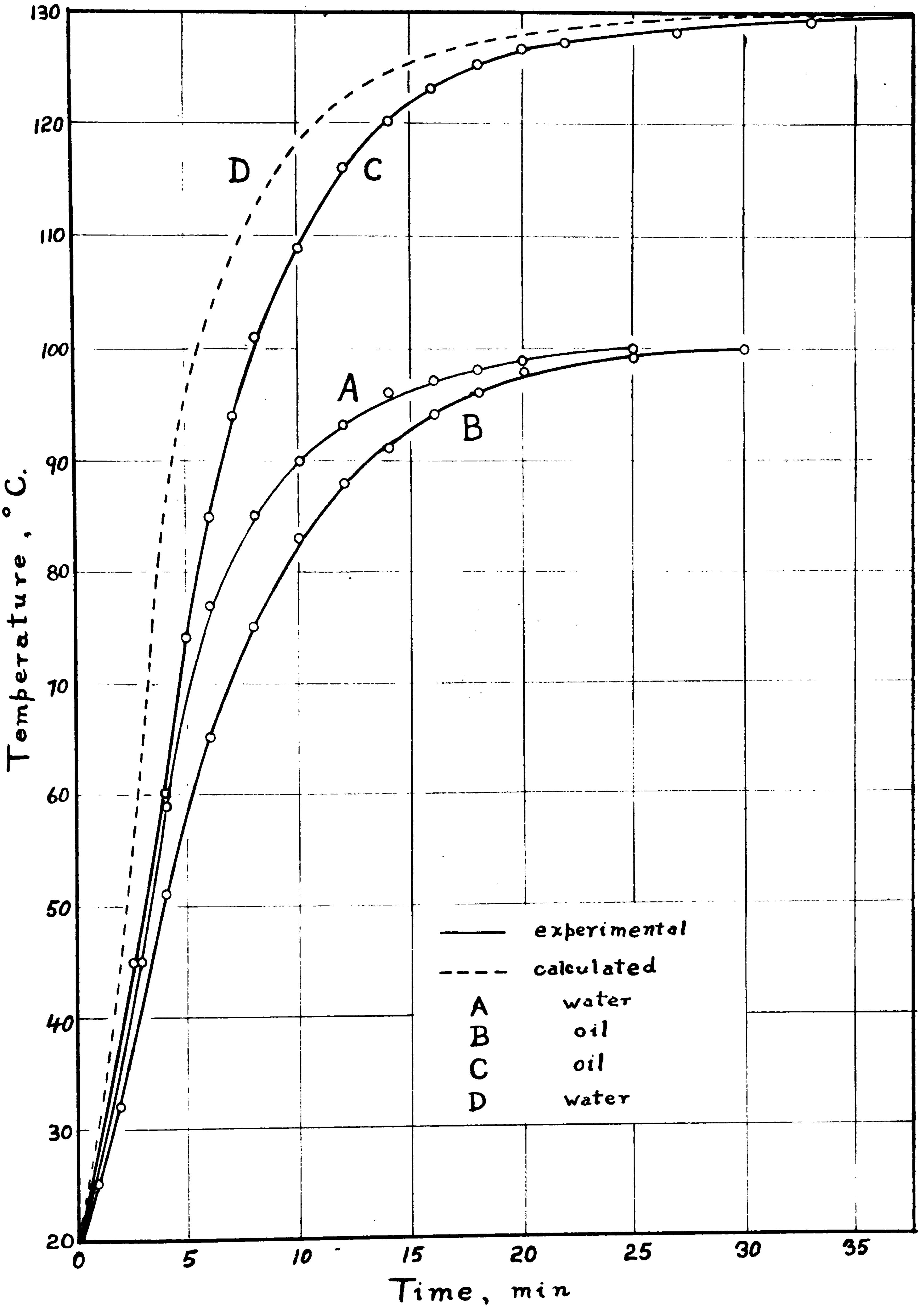


Fig. 17. Heating curves for the pyrex bomb digester and brass casing with thermostat at 100° and 130°C.

$$\theta_1 = \int_0^t 2^{tx/10}\, dt \quad \ldots\ldots\ldots \quad (9)$$

where θ_1 = the equivalent time of cooking at the initial temperature "T_1",

x = the rate of heating, degrees per minute,

t = the time of heating, minutes.

On integration, Equation (9) becomes:

$$\theta_1 = \frac{2^{tx/10} - 1}{0.0693\, x} \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

It was desired to know the equivalent time of cooking (θ_2) at the final temperature (T_2) for the heating period. This can be obtained from the relation:

$$\theta_2 = \frac{\theta_1}{2^{(T_2 - T_1)/10}}$$

$$= \frac{2^{tx/10} - 1}{0.0693\, x \,.\, 2^{(T_2 - T_1)/10}} \quad \ldots \quad (11)$$

In this way, the amount of cooking done during the heating period can be calculated in terms of the time required to do the same amount of cooking at the final temperature (T_2). This is independent of the absolute velocity of delignification, and hence the same time correction can be applied to every cook having the same temperature schedule, no matter what the liquor composition.

Since the heating curve (Fig. 17, D) is exponential, it was divided into five approximately linear sections and Equation (14) applied to each in turn. In this manner, the amount of cooking done during the heating period was calculated to be equivalent to 22 minutes cooking at 130°C. The time required for the bombs to reach 130°C. (from Fig. 17, D) is 35 minutes. Therefore, the time correction is 13 minutes, or 0.22 hours, which is to be subtracted from the observed time the bombs were in the bath.

For the one cook carried out at 110°C., the time correction was calculated in the same manner to be -0.18 hours. For temperatures below 110°C., the metal casings for the bombs were not used, and the length of the cook was sufficiently long that the time correction was negligible. No correction was necessary for cooking taking place during cooling after removal from the bath, since the temperature of the bombs dropped so rapidly when quenched in water that cooking was almost instantly stopped.

RESULTS AND DISCUSSION (PART II)

A. The Effect of Composition of Calcium Base Sulphite Liquor

The rate of delignification of spruce wood in calcium base sulphite liquor was determined at 130°C., over a concentration range of initially 0.25 to 2.0% combined, and 2 to 14% total sulphur dioxide, limited only by the solubility restrictions of the system. Use was made of the data of Gishler and Maass (24) on precipitation temperatures, to avoid the use of liquor concentrations which would result in the precipitation of calcium sulphite during cooking. Unfortunately, the precipitation temperatures were much too high, a fact which has since been confirmed by Beazley (3,4). Hence, precipitation did occur unexpectedly in several runs, making the true concentration at 130°C. uncertain in these cases.

The data from 23 runs are reported in Table 20, arranged in order of increasing total sulphur dioxide in each series of combined. It is observed that in any particular run, the combined sulphur dioxide decreases slightly throughout the cook due to a small consumption of lime. The total sulphur dioxide would also show a slight but regular decrease, if the initial concentrations were exactly the same in every bomb. The discrepancies are due to the fact that there is always a small loss of gas when pouring the liquor, and the bombs were not always cooked in the same order in which they were filled.

TABLE 20

The Effect of Composition of Calcium Base Sulphite Liquor on the Rate of Delignification of Spruce Wood and Yield of Pulp

Wood:- spruce meal, 40-100 mesh. Density 0.43. Extracted in Soxhlet 12 hr., alcohol-benzene (1:2). Lignin 27.5%, extracted wood basis.

Cooking:- Pyrex bombs, 130°C.

I	II	III	IV	V	VI	VII	VIII
Time in bath (un-corr.), hours	Comb. SO_2, %	Total SO_2 (un-corr.), %	Total SO_2 (corr.), %	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood
Series A Initial combined sulphur dioxide, 0.25%.							
Run No. 75. Average total sulphur dioxide, 1.70%.							
3.00	0.21	1.76	1.75	70.6	53.5	24.3	17.1
6.00	0.17	1.75	1.74	63.0	50.4	19.9	12.6
8.50	0.15	1.72	1.70	55.3	49.6	13.9	7.67
11.00	0.14	1.72	1.71	51.3	46.6	9.07	4.65
13.50	0.15	1.69	1.67	49.0	46.2	5.61	2.75
16.00	0.12	1.64	1.63	46.8	45.0	3.74	1.75
Average	0.16	1.71	1.70				
Run No. 72. Average total sulphur dioxide, 3.68%.							
1.50	0.22	3.68	3.65	71.5	54.6	23.7	16.9
3.00	0.20	3.74	3.71	59.7	50.3	15.7	9.36
4.00	0.19	3.74	3.71	53.3	48.5	8.94	4.76
5.00	0.18	3.71	3.68	50.2	47.2	5.16	2.69
6.50	0.17	3.72	3.69	47.3	46.1	2.59	1.22
8.00	0.15	3.68	3.65	46.5	45.8	1.52	0.71
Average	0.18	3.71	3.68				

TABLE 20 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 71. Average total sulphur dioxide, 5.07%.							
1.00	0.22	5.06	5.04	72.0	53.9	25.1	18.1
2.00	0.19	5.08	5.05	62.3	51.0	18.2	11.3
3.00	0.19	5.13	5.11	53.2	48.3	9.13	4.86
4.00	0.17	5.14	5.13	49.0	46.9	4.23	2.07
5.00	0.15	5.08	5.06	47.2	46.0	2.59	1.22
6.00	0.15	5.10	5.05	45.3	44.5	1.75	0.79
Average	0.18	5.10	5.07				
Run No. 73. Average total sulphur dioxide, 6.92%.							
1.00	0.21	6.94	6.90	68.8	52.8	23.2	16.0
2.00	0.19	6.94	6.90	54.8	48.8	11.0	6.00
2.75	0.18	7.04	6.98	49.5	46.9	5.21	2.58
3.50	0.15	6.98	6.94	47.9	46.6	2.73	1.31
4.25	0.14	6.94	6.87	46.7	45.9	1.65	0.77
5.00	0.12	6.98	6.91	45.9	45.4	1.14	0.53
Average	0.17	6.97	6.92				
Series B Initial combined sulphur dioxide, 0.5%.							
Run No. 60. Average total sulphur dioxide, 2.57%.							
2.00	0.43	2.67	2.66	73.5	57.7	21.6	15.8
4.00	0.40	2.64	2.63	65.2	55.3	15.2	9.89
6.00	0.38	2.59	2.57	56.5	51.7	8.42	4.75
8.00	0.37	2.55	2.55	52.6	50.3	4.32	2.27
10.00	0.36	2.47	2.45	51.3	50.1	2.30	1.18
Average	0.39	2.58	2.57				
Run No. 59. Average total sulphur dioxide, 4.10%.							
1.50	0.45	4.20	4.17	71.3	56.7	20.5	14.6
3.00	0.42	4.18	4.17	60.7	53.4	12.0	7.27
4.00	0.40	4.15	4.12	53.8	50.4	6.34	3.41
5.00	0.40	4.08	4.07	50.9	48.9	3.96	2.02
6.00	0.39	4.05	4.04	49.1	48.2	1.92	0.94
7.00	0.39	4.02	4.00	47.3	46.7	1.17	0.55
Average	0.41	4.11	4.10				

TABLE 20 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 63. Average total sulphur dioxide, 5.59%.							
1.00	0.44	5.50	5.48	73.4	56.5	23.0	16.9
2.00	0.42	5.62	5.60	62.9	53.9	14.3	8.99
3.00	0.42	5.76	5.71	53.7	50.2	6.51	3.50
4.00	0.38	5.62	5.62	49.6	48.2	2.88	1.43
5.50	0.35	5.62	5.55	46.8	45.7	1.13	0.53
Average	0.40	5.62	5.59				
Run No. 62. Average total sulphur dioxide, 7.34%.							
0.75	0.44	7.51	7.48	74.0	57.4	22.4	16.6
1.50	0.43	7.45	7.42	62.6	53.8	14.1	8.83
2.00	0.42	7.26	7.18	57.0	52.0	8.87	5.05
3.00	0.38	7.32	7.29	49.5	48.1	2.81	1.39
3.75	0.35	7.36	7.33	48.6	47.8	1.55	0.75
Average	0.40	7.38	7.34				
Run No. 74. Average total sulphur dioxide, 9.67%.							
0.75	0.46	9.73	9.63	74.2	58.9	20.4	15.3
1.50	0.42	9.77	9.72	59.5	52.9	11.1	6.59
2.00	0.41	9.69	9.59	52.6	50.0	4.88	2.57
2.50	0.42	9.79	9.79	49.6	48.7	1.76	0.87
3.00	0.39	9.69	9.59	48.7	48.3	0.91	0.44
3.50	0.38	9.85	9.70	47.8	47.5	0.60	0.29
Average	0.41	9.75	9.67				
Run No. 66. Average total sulphur dioxide, 12.48%.							
0.50	0.48	12.10	12.03	76.6	59.2	22.8	17.4
1.00	0.43	-	-	63.7	54.7	14.1	9.00
1.25	0.42	12.50	12.43	59.7	53.5	10.4	6.18
2.00	0.40	12.55	12.42	50.5	49.3	2.37	1.20
2.50	0.42	12.88	12.71	49.0	48.4	1.28	0.63
3.00	0.37	12.98	12.84	47.7	47.2	0.92	0.44
Average	0.42	12.60	12.48				

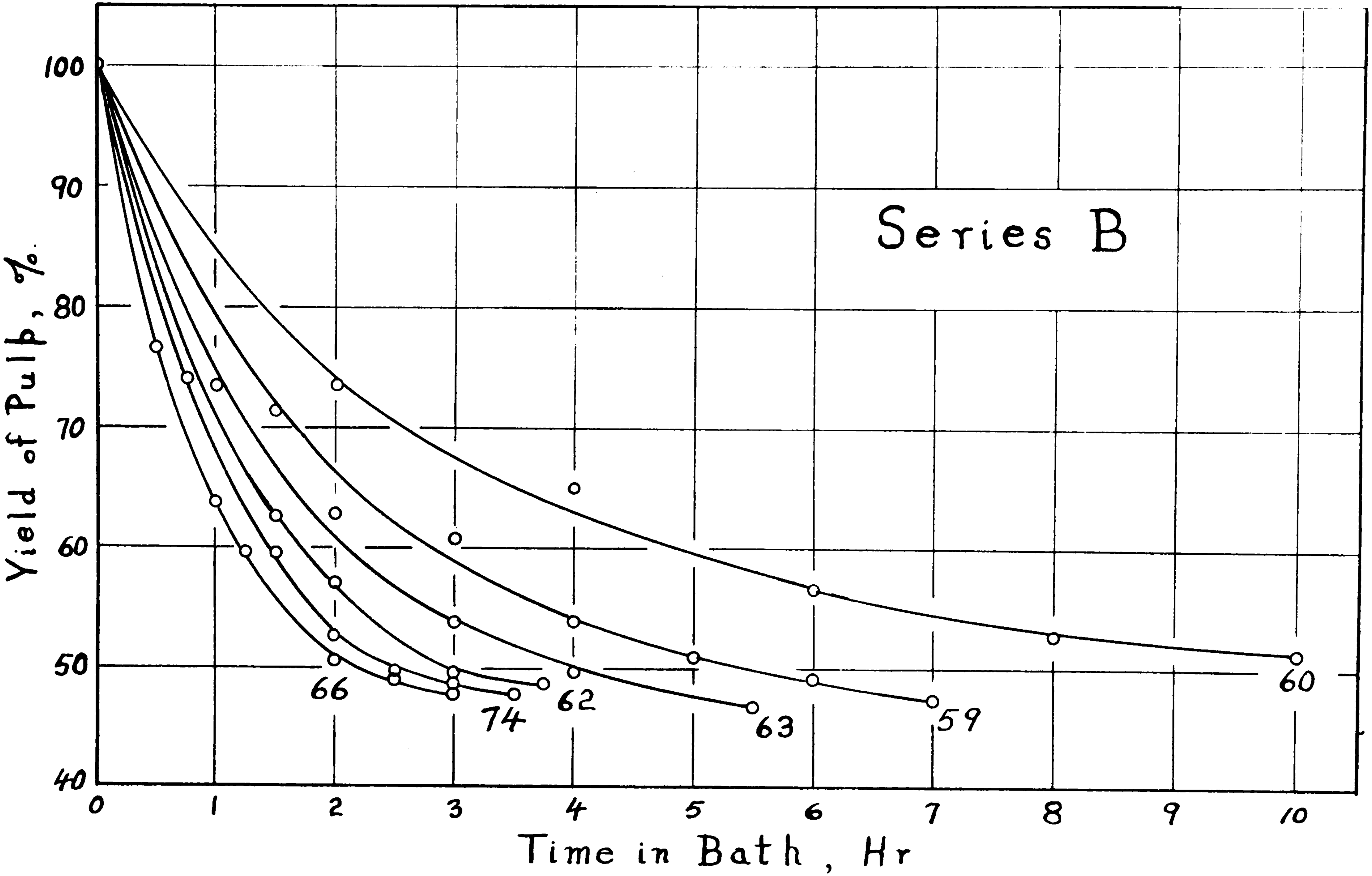


Fig. 18. The effect of the free sulphur dioxide concentration on the yield of pulp. Calcium base sulphite liquor; average combined sulphur dioxide 0.40%; temperature 130°C.

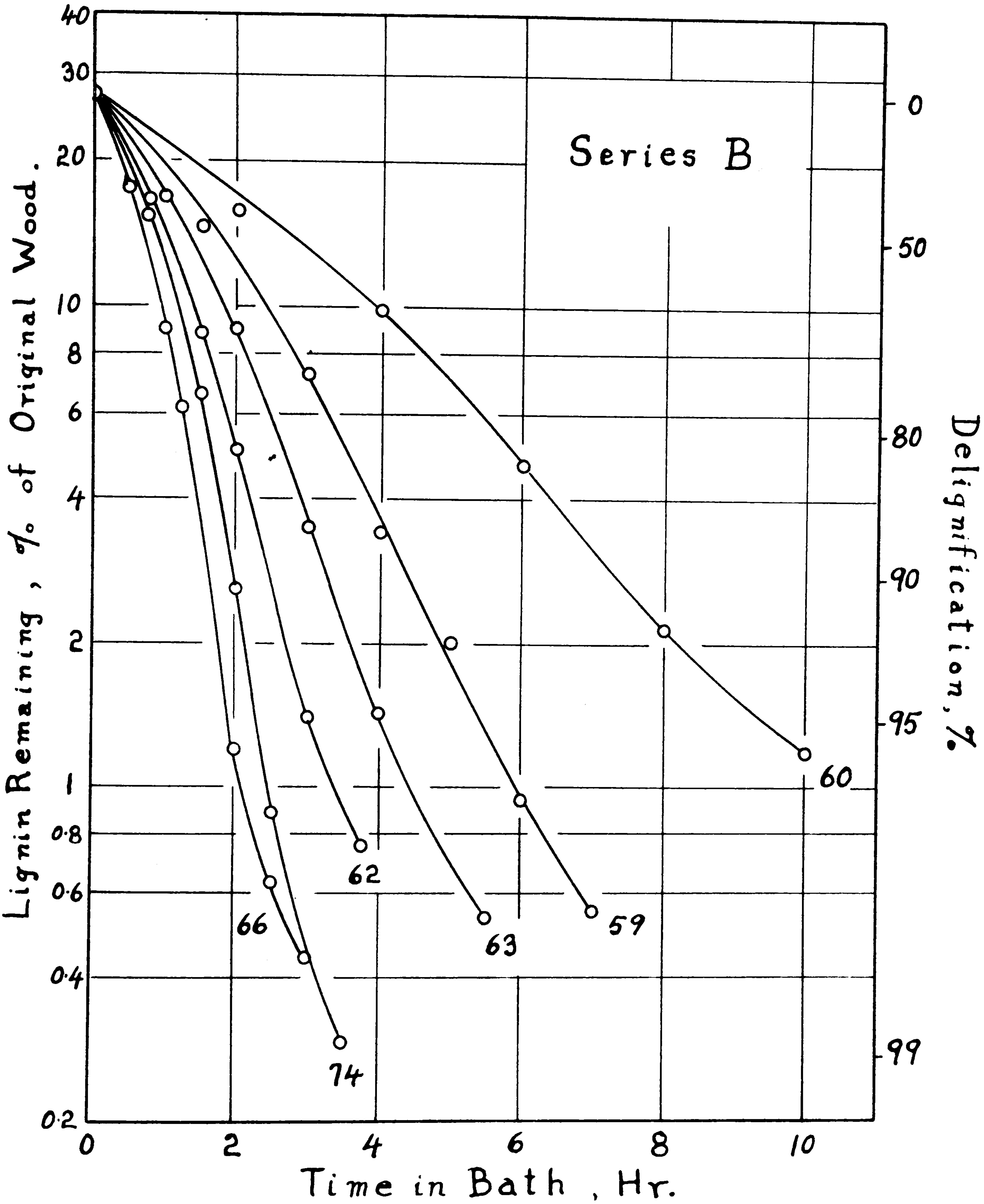


Fig. 19. The effect of the free sulphur dioxide concentration on the rate of delignification of spruce wood. Calcium base sulphite liquor; average combined sulphur dioxide 0.40%; temperature 130°C.

TABLE 20 (continued)

I	II	III	IV	V	VI	VII	VIII
Series C Initial combined sulphur dioxide, 1.0%.							
Run No. 56. Average total sulphur dioxide, 3.27%.							
1.50	0.92	3.40	3.38	79.3	62.4	21.4	16.9
3.00	0.90	3.34	3.32	70.6	59.2	16.2	11.4
4.50	0.90	3.28	3.25	64.6	56.9	12.0	7.74
6.00	0.88	3.30	3.28	57.9	54.1	6.58	3.81
7.50	0.81	3.23	3.21	54.6	52.4	3.98	2.17
10.00	0.81	3.21	3.19	51.3	50.7	1.24	0.63
Average	0.87	3.29	3.27				
Note:- A small amount of calcium sulphite precipitated.							
Run No. 51. Average total sulphur dioxide, 4.14%.							
1.50	0.95	4.21	4.17	75.3	60.5	19.7	14.8
3.00	0.94	4.22	4.21	64.5	56.2	12.8	8.25
4.00	0.92	4.16	4.15	60.5	55.2	8.67	5.25
5.00	0.90	4.18	4.17	57.0	53.8	5.65	3.22
6.00	0.89	4.14	4.12	53.3	51.5	3.46	1.84
8.00	0.86	4.06	4.04	51.6	50.9	1.44	0.74
Average	0.91	4.16	4.14				
Run No. 77. Average total sulphur dioxide, 4.87%.							
1.50	0.96	4.90	4.87	73.3	60.3	17.8	13.0
3.00	0.93	4.92	4.89	62.8	56.8	9.53	5.99
4.00	0.93	4.92	4.89	57.1	54.0	5.38	3.07
5.00	0.91	4.90	4.89	53.4	-	-	-
6.25	0.90	4.86	4.84	51.5	50.8	1.42	0.73
7.00	0.89	4.86	4.82	50.7	50.2	0.96	0.49
Average	0.92	4.89	4.87				
Run No. 76. Average total sulphur dioxide, 5.88%.							
1.00	0.95	5.86	5.84	76.0	59.9	21.2	16.1
2.00	0.93	5.94	5.92	65.5	57.6	12.1	7.94
3.00	0.91	5.94	5.90	57.6	53.9	6.32	3.70
4.00	0.89	5.92	5.90	53.2	51.9	2.37	1.26
5.00	0.88	5.92	5.89	51.3	50.6	1.41	0.72
6.00	0.88	5.90	5.85	49.7	49.3	0.87	0.43
Average	0.91	5.91	5.88				

TABLE 20 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 52. Average total sulphur dioxide, 5.97%.							
1.00	0.96	6.18	6.12	75.8	59.7	21.2	16.1
2.00	0.96	6.12	6.08	65.1	56.6	13.1	8.52
3.00	0.93	5.98	5.93	57.5	54.0	6.11	3.51
4.00	0.92	5.96	5.92	54.0	52.5	2.79	1.51
5.50	0.89	5.82	5.78	50.8	50.2	1.24	0.63
Average	0.93	6.01	5.97				
Run No. 53. Average total sulphur dioxide, 8.05%.							
0.75	0.96	8.34	8.27	77.0	60.0	22.1	17.0
1.75	0.92	8.06	7.98	63.0	55.4	12.1	7.62
2.50	0.92	8.10	7.98	55.9	53.2	4.93	2.75
3.25	0.89	8.08	8.00	52.2	51.0	2.31	1.21
4.00	0.87	8.16	8.08	50.1	49.4	1.42	0.71
Average	0.91	8.15	8.05				
Run No. 55. Average total sulphur dioxide, 10.65%.							
0.50	0.96	11.06	10.90	81.0	61.4	24.2	19.6
1.00	0.92	11.06	10.92	69.6	57.2	17.8	12.4
1.50	0.90	10.88	10.75	62.0	55.2	10.96	6.80
2.00	0.83	10.72	10.59	55.7	52.9	4.96	2.76
2.50	0.84	10.80	10.61	52.1	50.8	2.55	1.33
3.00	0.78	10.36	10.15	50.4	49.4	1.93	0.97
Average	0.87	10.81	10.65				
Run No. 61. Average total sulphur dioxide, 13.92%.							
0.50	0.98	13.78	13.59	77.7	61.3	21.1	16.4
1.00	0.94	13.92	13.81	64.5	56.4	12.6	8.10
1.50	0.89	14.10	13.80	57.0	53.7	5.71	3.26
2.00	0.90	14.48	14.37	52.2	51.2	1.97	1.02
2.50	0.88	14.18	14.03	50.0	49.5	1.04	0.52
Average	0.92	14.09	13.92				

TABLE 20 (continued)

Series D Initial combined sulphur dioxide, 1.5%.

Run No. 67. Average total sulphur dioxide, 7.68%.

I	II	III	IV	V	VI	VII	VIII
1.00	1.50	7.74	7.71	74.7	61.6	17.5	13.1
2.00	1.45	7.78	7.75	63.5	58.1	8.47	5.37
2.50	1.43	7.68	7.68	58.3	55.4	4.94	2.88
3.25	1.40	7.64	7.57	54.0	53.0	1.76	0.95
Average	1.44	7.71	7.68				

Note:- A small amount of calcium sulphite precipitated.

Run No. 68. Average total sulphur dioxide, 10.71%.

I	II	III	IV	V	VI	VII	VIII
0.78	1.44	10.72	10.62	77.0	62.7	18.5	14.3
1.50	1.42	10.69	10.66	63.5	-	-	-
2.00	1.37	10.73	10.60	57.1	54.4	4.71	2.70
2.50	1.35	10.88	10.80	53.5	52.5	1.81	0.97
3.00	1.35	10.92	10.79	51.5	50.9	1.13	0.58
3.50	1.35	10.88	10.78	50.0	49.6	0.77	0.38
Average	1.38	10.80	10.71				

Run No. 69. Average total sulphur dioxide, 14.04%.

I	II	III	IV	V	VI	VII	VIII
0.50	1.45	13.88	13.77	81.7	63.8	21.9	17.9
1.00	1.41	14.12	14.05	69.8	60.5	13.4	9.31
1.50	1.40	14.12	13.97	59.4	55.6	6.47	3.84
2.00	1.37	14.16	14.12	54.0	52.9	2.05	1.11
2.50	1.38	14.32	14.21	51.9	51.4	0.89	0.46
3.00	1.34	14.28	14.10	50.6	50.3	0.60	0.30
Average	1.39	14.15	14.04				

Series E Initial combined sulphur dioxide, 2.0%.

Run No. 64. Average total sulphur dioxide, 11.38%.

I	II	III	IV	V	VI	VII	VIII
0.50	1.82	11.28	11.23	85.8	68.1	20.7	17.7
1.00	1.74	11.50	11.39	72.1	61.4	14.8	10.7
2.00	1.74	11.58	11.53	57.0	55.2	3.40	1.94
3.00	1.74	11.53	11.37	51.6	51.0	1.15	0.59
Average	1.76	11.47	11.38				

Note:- Some calcium sulphite precipitated.

TABLE 20 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 65. Average total sulphur dioxide, 13.46%.							
0.50	1.88	13.40	13.33	81.8	65.5	20.0	16.3
1.00	1.83	13.50	13.43	69.7	61.1	12.4	8.65
1.50	1.89	13.62	13.47	60.9	56.7	6.86	4.18
2.25	1.79	13.56	13.38	53.6	52.6	1.85	0.99
2.75	1.82	13.85	13.70	51.9	51.4	1.04	0.54
Average	1.84	13.59	13.46				

Note:- A small amount of calcium sulphite precipitated.

However, the deviations from the mean value for each cook are small. The correction for sulphur dioxide lost to the vapor phase, although never large, increases with the concentration of the liquor.

The yield of pulp for each run was plotted against the observed time of cooking, as illustrated with Series B, Fig. 18. The logarithm of the lignin remaining (as percent of the original wood) was plotted for each run against the observed time of cooking, as illustrated.with Series B, Fig. 19. It is seen that the delignification curves all deviate somewhat from the first order relation as reported by Yorston (73) and by Corey and Maass (18). Hence, no attempt was made to estimate velocity constants, and the time required to remove 90% of the lignin was taken as the best measure of the rate.

A complete summary of the experimental and calculated data for all runs is given in Table 21. The uncorrected times to 80, 90 and 95% delignification for each run were read from the

Table 21

SUMMARY OF THE EFFECT OF COMPOSITION OF CALCIUM BASE SULPHITE LIQUOR ON THE DELIGNIFICATION OF SPRUCE WOOD AT 130°C.

Series No.	Run No.	Average final concentration of sulphur dioxide (corrected)					80% delignification		90% delignification		95% delignification		pH of liquor at 130°C.	Partial pressure sulphur dioxide 130°C., cm.	Time to 90% delignification, (corrected) hours = $t_{90\%}$	Rate of delignification = $1/t_{90\%}$
		Combined, %	Total, %	Free (total-comb.), %	Total-1.5 x comb., %	Excess (total-2 x comb.), %	Time (uncorr.), hours	Yield of pulp, %	Time (uncorr.), hours	Yield of pulp, %	Time (uncorr.), hours	Yield of pulp, %				
A	75	0.16	1.70	1.54	1.46	1.38	10.15	52.5	13.50	49.0	17.5	45.7	2.35	116	13.28	0.075
	72	0.18	3.68	3.50	3.41	3.32	3.80	54.3	4.96	50.2	6.27	47.6	2.03	286	4.74	0.211
	71	0.18	5.07	4.89	4.80	4.71	2.90	54.1	3.63	50.2	4.75	47.6	1.94	414	3.41	0.293
	73	0.17	6.92	6.75	6.67	6.58	2.09	54.0	2.70	49.8	3.44	47.9	1.86	600	2.48	0.403
	Av.	0.17						53.7		49.8		47.2				
B	60	0.39	2.57	2.18	1.98	1.79	5.62	57.8	7.48	53.5	9.45	51.0	2.53	164	7.26	0.138
	59	0.41	4.10	3.69	3.48	3.28	3.40	57.0	4.45	52.5	5.45	50.0	2.30	318	4.23	0.237
	63	0.40	5.59	5.19	4.99	4.79	2.55	57.5	3.26	52.3	4.05	49.4	2.21	466	3.04	0.329
	62	0.40	7.34	6.94	6.74	6.54	1.94	57.6	2.48	52.8	3.01	49.5	2.12	642	2.26	0.443
	74	0.41	9.67	9.26	9.05	8.85	1.61	57.8	1.97	53.1	2.27	50.7	2.00	878	1.75	0.572
	66	0.42	12.48	12.06	11.85	11.64	1.30	58.5	1.62	54.2	1.92	51.2	-	1164	1.40	0.715
	Av.	0.40						57.7		53.1		50.3				
C	56*	0.87	3.27	2.40	1.96	1.53	5.10	61.0	6.90	55.6	8.52	53.0	2.80	178	6.68	0.150
	51	0.91	4.14	3.23	2.78	2.32	3.90	60.8	5.30	56.0	6.60	53.0	2.66	262	5.08	0.197
	77	0.92	4.87	3.95	3.49	3.03	3.13	62.0	4.16	56.4	5.20	53.0	2.56	330	3.94	0.254
	76	0.91	5.88	4.97	4.52	4.06	2.50	61.0	3.26	56.1	3.95	53.4	2.46	425	3.04	0.329
	52	0.93	5.97	5.04	4.58	4.11	2.52	60.6	3.29	56.4	4.13	53.7	2.45	434	3.07	0.326
	53	0.91	8.05	7.14	6.69	6.23	2.02	60.2	2.50	55.9	3.10	52.7	2.29	628	2.28	0.438
	55	0.87	10.65	9.78	9.34	8.91	1.62	60.2	2.00	55.7	2.47	52.3	2.16	875	1.78	0.562
	61	0.92	13.92	13.00	12.54	12.08	1.22	61.0	1.59	55.9	1.88	53.1	-	1185	1.37	0.730
	Av.	0.90						60.8		56.0		53.0				
D	67*	1.44	7.68	6.24	5.52	4.80	1.97	63.5	2.53	57.8	3.00	54.8	-	-	2.31	0.433
	68	1.38	10.71	9.33	8.64	7.95	1.57	62.5	1.99	57.2	2.32	54.5	-	-	1.77	0.565
	69	1.39	14.04	12.65	11.95	11.26	1.31	63.0	1.65	57.5	1.92	54.6	-	-	1.43	0.700
	Av.	1.40						63.0		57.5		54.6				
E	64*	1.76	11.38	9.62	8.74	7.86	1.45	64.3	1.82	59.0	2.20	55.6	-	-	1.60	0.625
	65*	1.84	13.46	11.62	10.70	9.78	1.27	64.5	1.68	58.5	2.05	55.0	-	-	1.46	0.685
	Av.	1.80						64.4		58.7		55.3				

J.M.C. 5/3/38.

* Some calcium sulphite precipitated.

delignification curves, and the yields of pulp at the corresponding times were read from the yield curves. The time correction does not affect the yields of pulp taken at a given lignin content.

1. The Effect of Liquor Composition on the Yield of Pulp

An inspection of Table 21 shows that the yield of pulp at a given lignin content increases rapidly with the combined, but is virtually independent of the free sulphur dioxide over the whole concentration range. This is brought out in Fig. 20, in which the average yield for each series, taken at 80, 90 and 95% delignification, is plotted against the average combined sulphur dioxide.

This effect of the combined sulphur dioxide is substantiated qualitatively by the results of Hägglund and Nihlen (34) and Mitchell and Yorston (53), although Miller and Swanson (52), state that they could not show any variation in yield attributable to any of the factors in acid composition. It has generally been believed that a high sulphur dioxide content resulted in a loss in yield, owing to the greater acidity of the liquor. The contradictions in the literature are no doubt due to lack of uniformity in the methods used and the fact that the yields, in some cases, were not compared at the same lignin content.

The effect of liquor composition on the yield of pulp may be explained on the assumption that cellulose degradation at a given temperature is governed by the hydrogen ion concentration

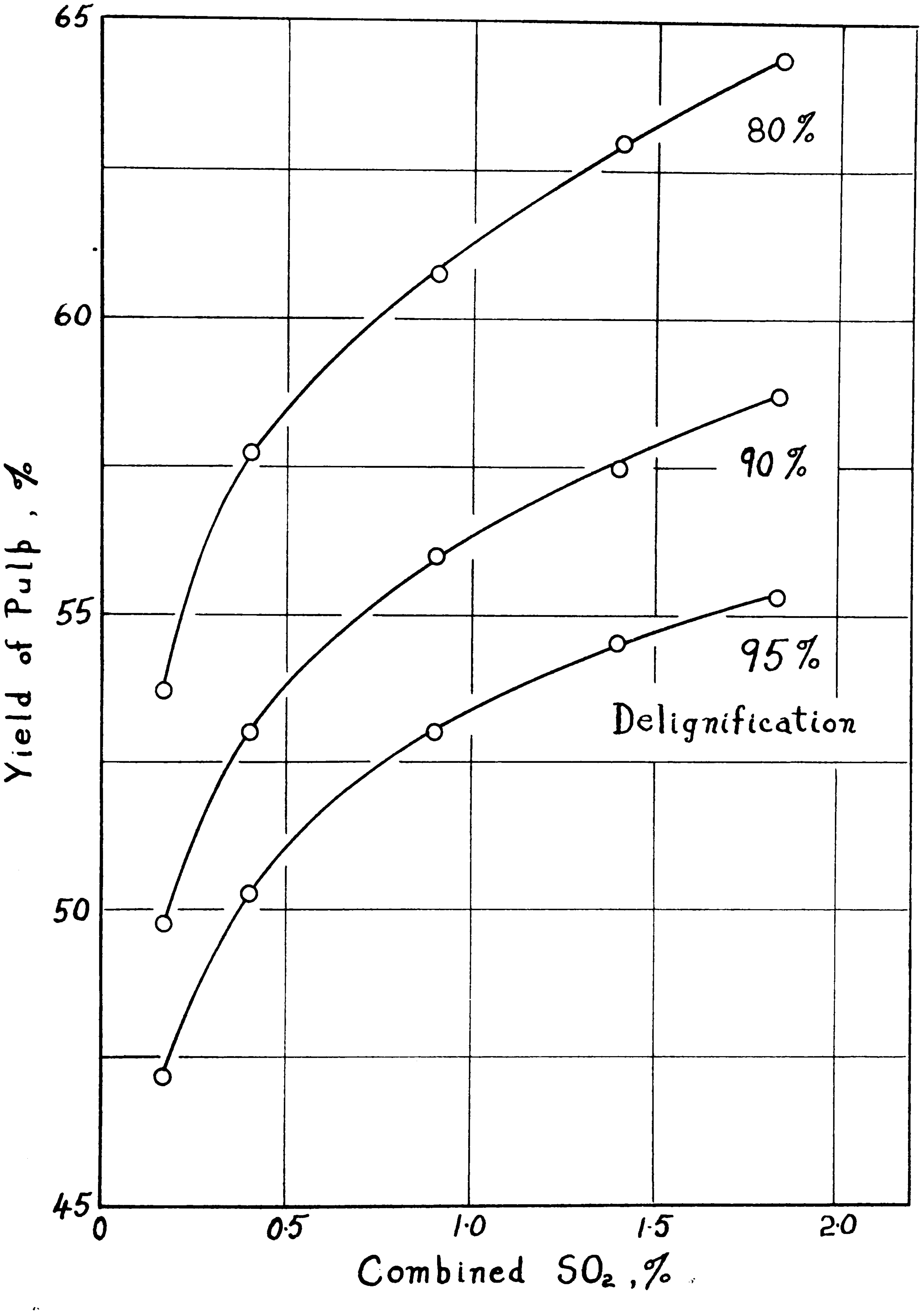


Fig. 20 The effect of the combined sulphur dioxide concentration on the yield of pulp. Calcium base sulphite liquor, 130°C.

of the liquor. At constant free sulphur dioxide, the pH of the liquor increases with the concentration of the combined. In fact the pH curves for sulphite liquor of different lime concentrations, obtained by extrapolating the data of Gishler and Maass (23) to 130°C., are almost identical in shape with the yield curves in Fig. 20. That the yield should be independent of the free sulphur dioxide, even though the pH is not, is due to the fact that increased acidity is balanced by the decrease in time required for cooking.

It has thus been shown conclusively that under the conditions of these experiments, an increase in the free sulphur dioxide will not appreciably affect the yield of pulp, whereas an increase in the combined sulphur dioxide greatly improves the yield. The yields obtained with the liquors containing 0.9% or more of combined sulphur dioxide are distinctly better than those realized in mill practise. This is true, even allowing for the fact that our yields would be 1 to 2% lower if calculated on the unextracted wood basis. It may be suggested that the lower yields under mill conditions are due to the low concentration of combined sulphur dioxide prevailing toward the end of the cook. However, opinion is divided as to the effect of changes in the initial concentration of combined sulphur dioxide on the yield of pulp from a commercial digester.

2. The Effect of Liquor Composition on the Shape of the Delignification Curve

It was of interest to know whether the shape of the delignification curve was affected by the composition of the cooking liquor. In Table 21, the corrected time to 90% delignification ($t_{90\%}$), obtained by subtracting 0.22 hours from the observed time, is listed for each run. The rate of delignification is proportional to the reciprocal of this value ($1/t_{90\%}$). To make a satisfactory comparison between the delignification curves in Fig. 19, each observed time was corrected by subtracting 0.22 hours. These values were then multiplied by the arbitrary factor $6/t_{90\%}$ to make the curves coincident at the point corresponding to 90% removal of lignin.

The result is shown in Fig. 21, and it is seen that all the points fall on the one curve, irrespective of the composition of the liquor, except at low lignin values where analysis is less accurate. Series A and C were calculated and plotted in the same way, and were found to fit the same single curve. Since the shape of the delignification curve is independent of the liquor composition, it would seem that the mechanism of the reaction, whatever it may be, is the same with all of the liquors investigated. It should be pointed out that the initial curvature in Fig. 19 is smoothed out to some extent when the time correction is applied, as in Fig. 21. This is to be expected, since the rate of reaction will certainly increase with the rising temperature during the first few minutes when the bombs are being heated. However, even when this error is eliminated, there is still a considerable deviation from the unimolecular law.

The same data for Series B are replotted in Fig. 22 accord-

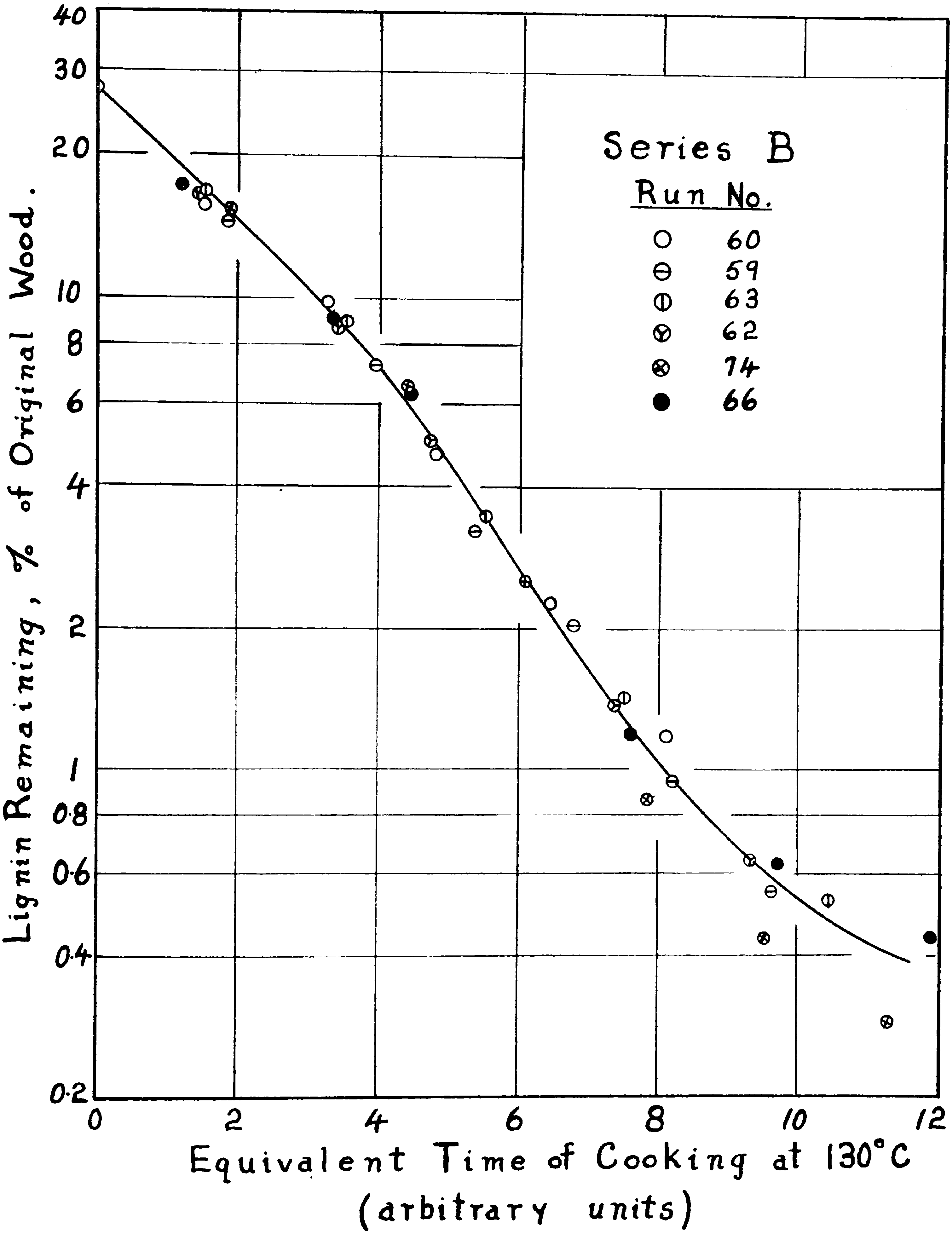


Fig. 21. The effect of the free sulphur dioxide concentration on the shape of the delignification curve. Calcium base sulphite liquor; average combined sulphur dioxide 0.40%; temperature 130°C.

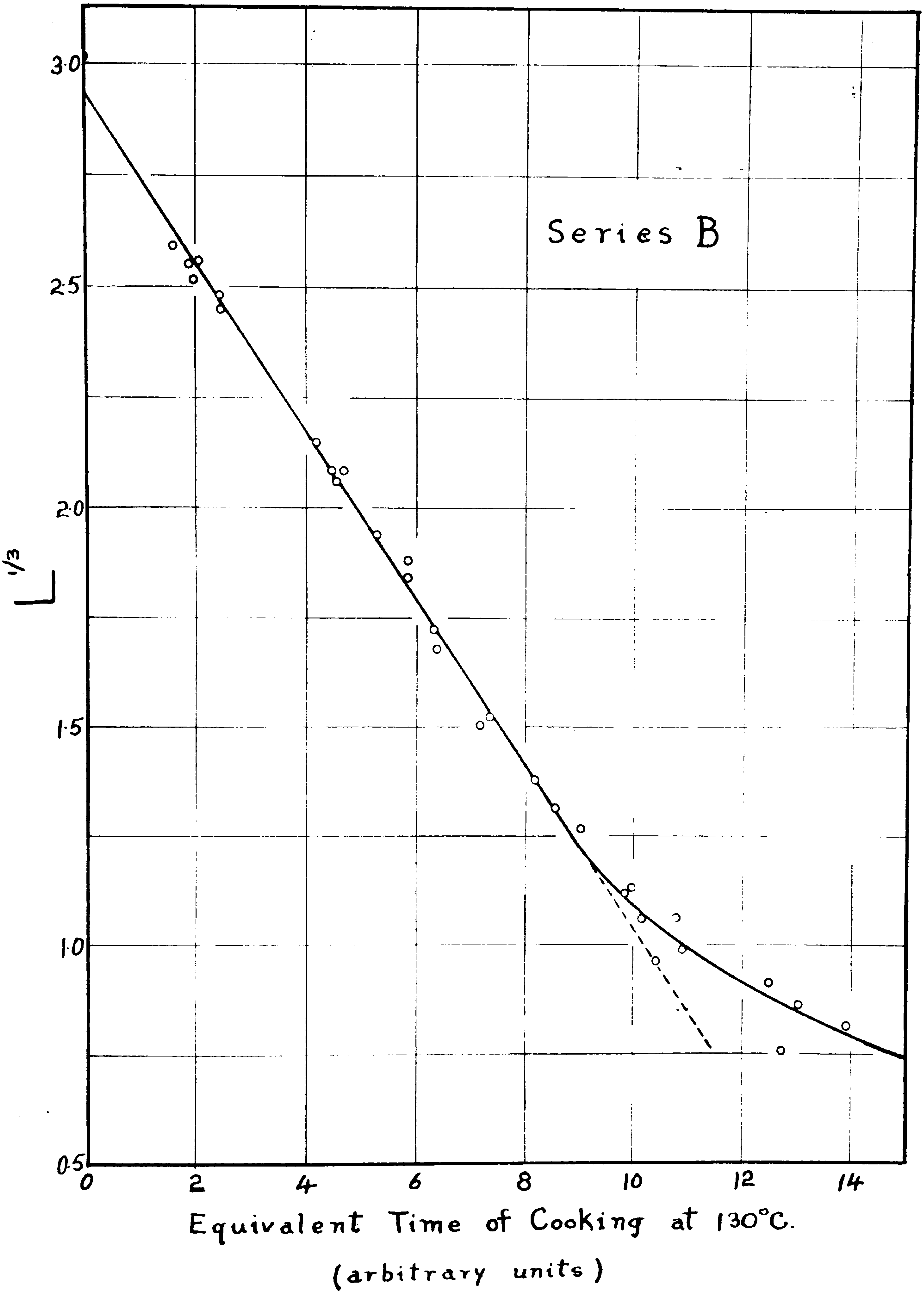


Fig. 22. The effect of the free sulphur dioxide concentration on the shape of the delignification curve. Calcium base sulphite liquor; average combined sulphur dioxide 0.40%; temperature 130°C.

ing to the relation derived in Part I, i.e., $L^{1/3}$ vs. time. It is observed that the experimental points fall more nearly on a straight line down to 95% delignification, than when plotted according to the first order relation. The best straight line, however, extrapolates to zero time at a lignin value about 1% lower than the lignin content of the original wood. Possible explanations for the departure from the straight line in the final stages of cooking have already been mentioned on page 81.

3. The Relation of the Free and Combined Sulphur Dioxide to the Rate of Delignification

The free sulphur dioxide (total-combined) and the excess sulphur dioxide (total- 2 x combined) were calculated for each run and are shown in Table 21. The rate of delignification ($1/t_{90\%}$) is plotted against the free sulphur dioxide in Fig. 23, and against the excess sulphur dioxide in Fig. 24 for each series of combined. Run Nos. 56, 64, 65 and 67 are omitted because of the uncertainty introduced by precipitation of calcium sulphite.

From these curves it is obvious that the free sulphur dioxide gives the best relation with the rate of delignification, since the points fall more closely on a single curve, irrespective of the concentration of combined sulphur dioxide. Furthermore, if the curve is extrapolated to zero concentration, it is seen that the rate becomes zero for zero free sulphur dioxide. In Fig. 24, on the other hand, the four series of combined sulphur dioxide give distinctly separate curves which cannot be

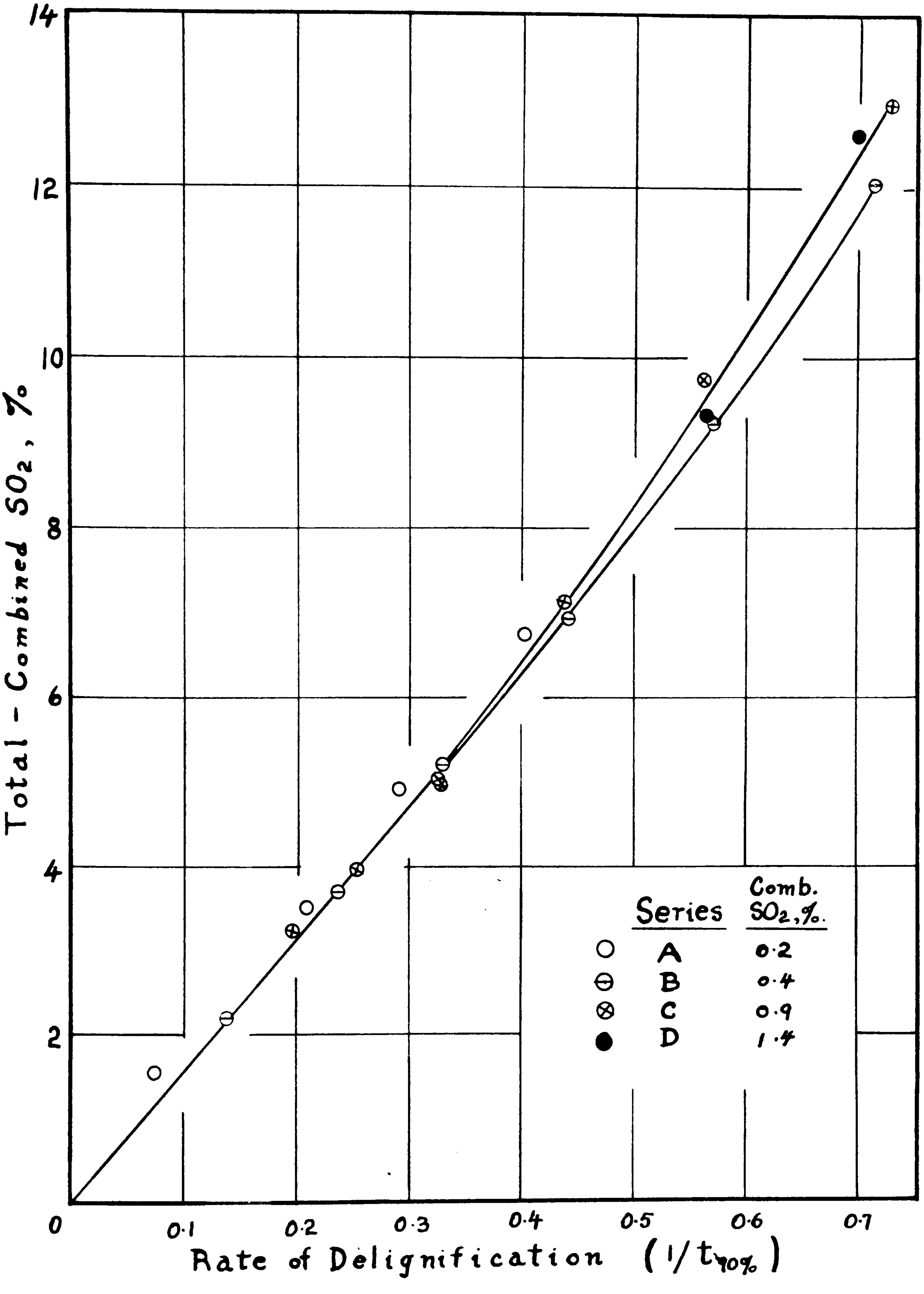


Fig. 23. The rate of delignification of spruce wood in calcium base sulphite liquor at 130°C. as a function of the free sulphur dioxide concentration.

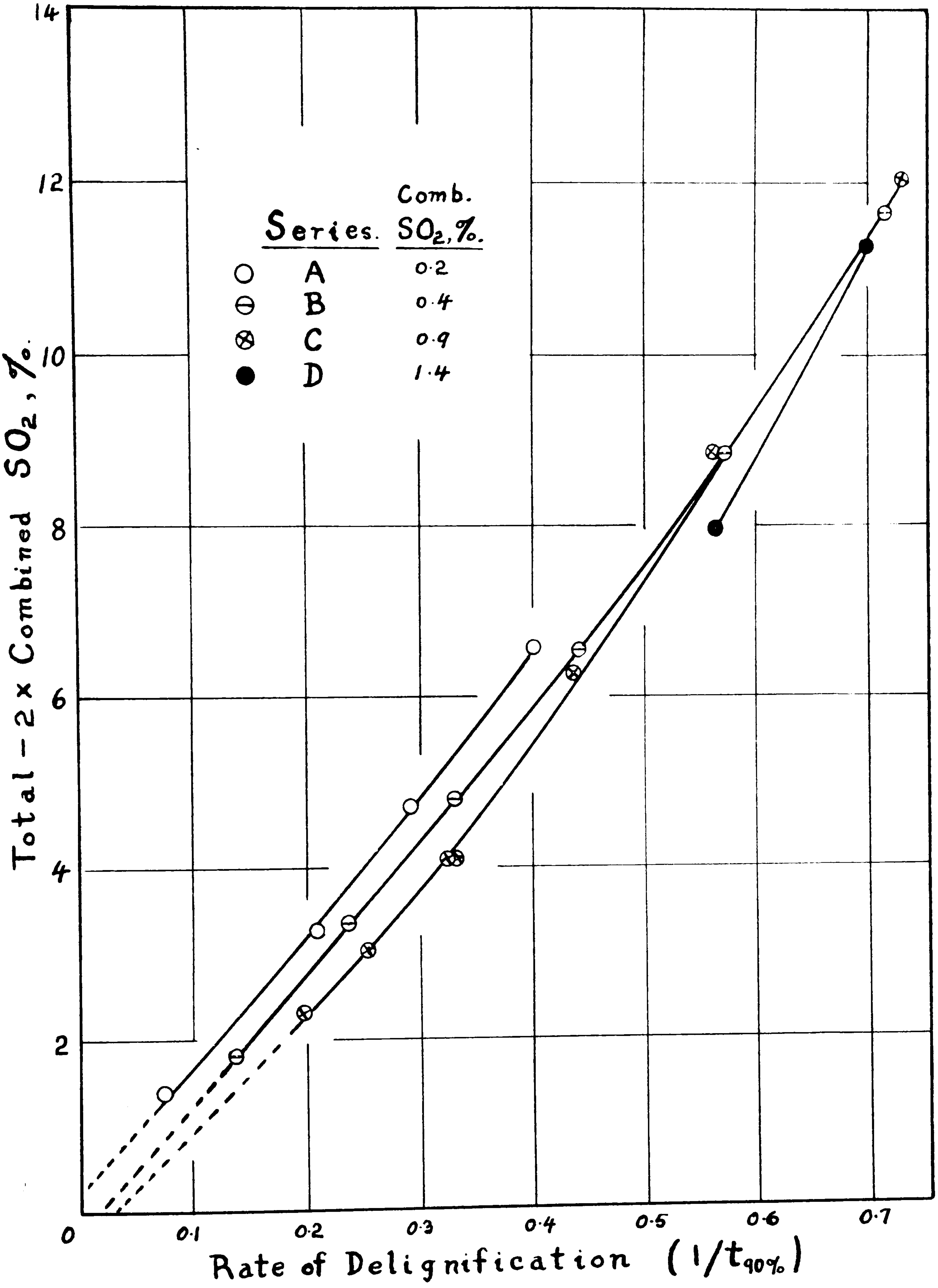


Fig. 24. The rate of delignification of spruce wood in calcium base sulphite liquor at 130°C. as a function of the "excess" sulphur dioxide concentration.

extrapolated to zero rate at zero concentration of excess sulphur dioxide. This proves that the excess sulphur dioxide of Miller and Swanson (52) is not the controlling factor in determining the rate of delignification

If the rate is plotted against the total - 1.5 x combined sulphur dioxide, as suggested by the equilibria data of Gishler and Maass (23), a relation is obtained midway between those illustrated in Figs. 23 and 24. No support can be given to such a relation from the evidence of actual cooking obtained here. The ordinary free sulphur dioxide appears to give the best measure of the rate of delignification, independently of the combined. The relation is not linear, but curves in a manner which shows that the increase in the rate of reaction with increase in free sulphur dioxide becomes less at the higher concentrations. This is in agreement with the results of McGovern (50). It must be remembered that the solubility restrictions of the calcium system prevent a wide variation in the combined sulphur dioxide, and the rate of delignification may not be determined by the concentration of free sulphur dioxide outside of this range of combined. In addition, it is only possible to cook satisfactorily with low concentrations of combined sulphur dioxide at high liquor ratios, because a definite quantity of lime, equal to about 5% of the weight of the wood, is required to neutralize the lignin sulphonic acids produced.

4. The Relation of the Partial Pressure of Sulphur Dioxide to the Rate of Delignification

Since the free sulphur dioxide was found to be the controlling factor in determining the rate of delignification in calcium base liquor, further calculations were of interest. The sulphur dioxide in solution which is not in combination with the lime is proportional to the partial pressure of the gas, and since the equilibrium relations between the different ionic and molecular species are so complex, the partial pressure of sulphur dioxide is a better measure of the true free than the value calculated from the analytical concentrations.

The most accurate measurements of the vapor pressure of calcium base sulphite liquor for various concentrations and temperatures have been carried out in this laboratory by Beazley (3). The partial pressure of sulphur dioxide at 130°C. was obtained for each liquor concentration where data were available. It was necessary to extrapolate to obtain the vapor pressures at concentrations greater than 6% total sulphur dioxide, but since the relation is linear except at low concentrations, the extrapolated values are considered accurate.

The partial pressures are given in Table 21 for Series A, B and C, and are plotted against the rate of cooking in Fig. 25. It is observed that all the points fall on the same curve, irrespective of the combined sulphur dioxide, and that the relation is much more uniform than that given by the analytical free sulphur dioxide in Fig. 23. It is also noticed that Fig. 25

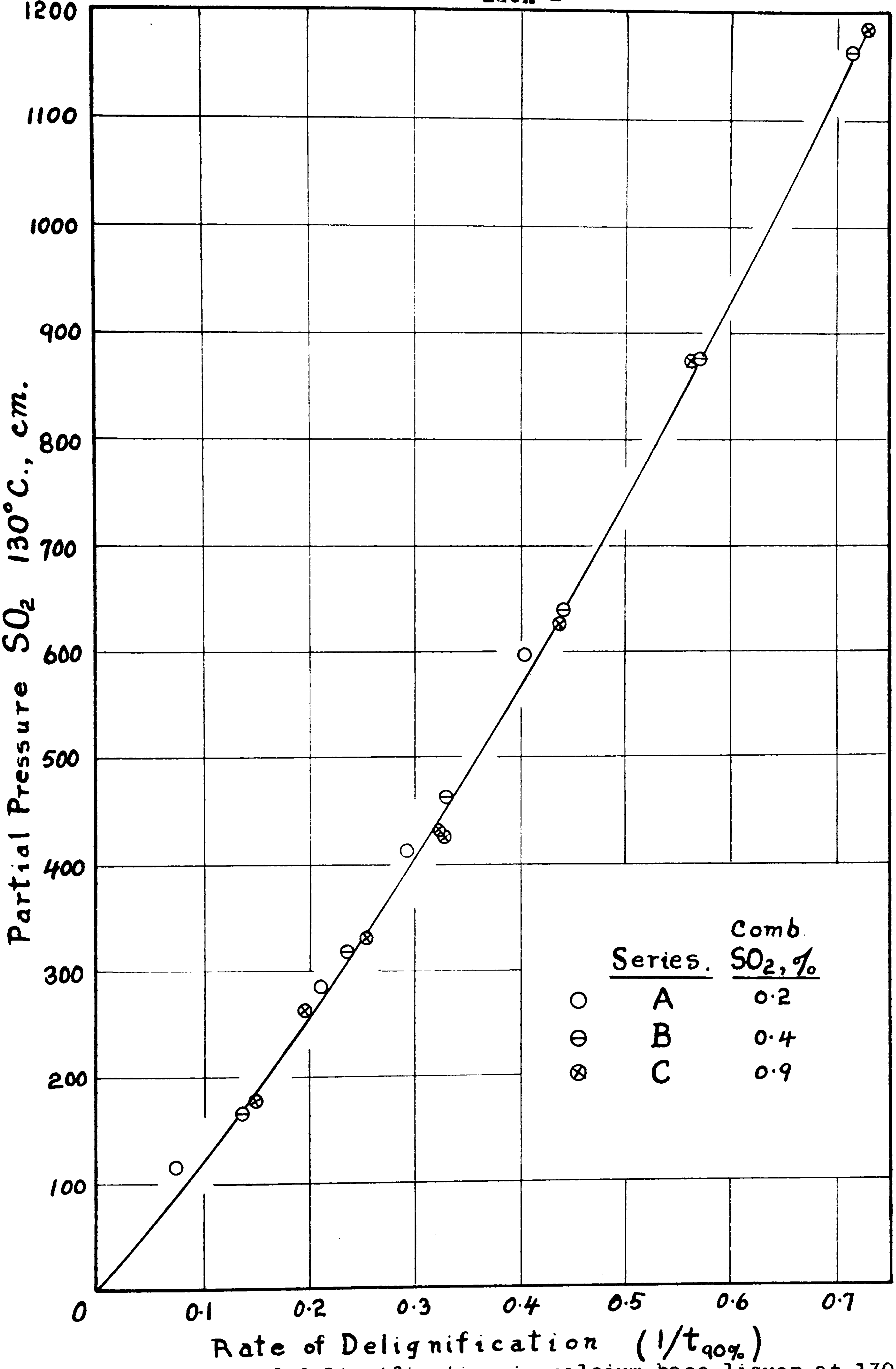


Fig. 25. The rate of delignification in calcium base liquor at 130°C as a function of the partial pressure of sulphur dioxide.

shows a very definite curvature, greater than any experimental error, such that the rate of cooking increases less rapidly at the higher partial pressures.

A consideration of the equilibria existing in sulphite liquor is necessary before any further explanation is offered. From a study of the system calcium oxide – sulphur dioxide – water, Gishler and Maass (23) have shown that the following relations hold:

$$P = K_1(SO_2) \qquad \ldots\ldots\ldots\ldots\ldots \quad (12)$$

where "P" is the partial pressure of sulphur dioxide gas. Also,

$$(SO_2)(H_2O) = K_2(H_2SO_3) \qquad \ldots\ldots\ldots\ldots \quad (13)$$

$$(H_2SO_3)K_3 = (H^+)(HSO_3^-) \qquad \ldots\ldots\ldots\ldots \quad (14)$$

from which it follows that

$$P = \frac{K_1K_2(H_2SO_3)}{(H_2O)} = \frac{K_1K_2(H^+)(HSO_3^-)}{K_3(H_2O)} \qquad \ldots\ldots\ldots \quad (15)$$

Equation (15) shows that, provided the concentration of water is considered constant, the partial pressure of sulphur dioxide is proportional to the concentration of sulphurous acid or the product of the concentration of the hydrogen and bisulphite ions. This relation is quite independent of the presence of lime. The addition of calcium monosulphite to the cooking liquor would not affect the rate of delignification, since the rate is independent of the combined sulphur dioxide when the free is constant. The decrease in hydrogen ion concentration must be compensated for by the increase in bisulphite ion concentration.

Apart from considerations of the mechanism of the reaction, this suggests that the active cooking agent in sulphite liquor is either sulphurous acid or the hydrogen and bisulphite ions together, and not either ion separately, as has frequently been claimed. This agrees with a statement of Miller and Swanson (52), that the removal of lignin is the result of the specific action of ionized sulphurous acid, and that the effective cooking action cannot be attributed to the bisulphite ion alone. Neither can it be attributed to the hydrogen ion alone, as claimed by Hägglund (28, 29, 30).

Gishler and Maass (24) have shown that the bisulphite ion in sulphite liquor is strongly buffered and increases only slightly with the concentration of free sulphur dioxide. Increase in the combined, however, causes a large increase in bisulphite. Hence according to Equation (15), an increase in the hydrogen ion concentration by the addition of sulphur dioxide, or an increase in the bisulphite ion concentration by the addition of both lime and sulphur dioxide, will increase the partial pressure of the gas as well as the rate of delignification. This explains the relation plotted in Fig. 25.

There are three possible explanations for the curvature observed in Fig. 25:

(a) At the high sulphur dioxide concentrations cooking is so rapid, that in spite of the high liquor ratio diffusion of the base into the wood-meal may not be fast enough to prevent a local high acidity, which might cause a slight burning and thus hinder cooking. Some evidence for this was found in a few cases, in which a slight discolouration of the wood-meal was observed at the bottom of the bomb. On the other hand, the relation appears to be much too uniform to be attributed to such an uncertain cause, and is substantiated qualitatively by the results of McGovern (50), already mentioned.

(b) A second possible explanation may be found by re-writing Equation (15):

$$P(H_2O) = K(H_2SO_3) = K'(H^+)(HSO_3^-) \quad \ldots\ldots \quad (16)$$

Since the liquors are concentrated, the water concentration cannot be considered strictly constant as in the case of dilute solutions. If the cooking action is due to sulphurous acid or the hydrogen and bisulphite ions together, Equation (16) shows that a linear relation with the rate would be obtained only by multiplying the partial pressure of sulphur dioxide by the molar concentration of water. Since this factor decreases with increase in the liquor concentration, it would tend to straighten the curve in Fig. 25.

An attempt to verify this was made by calculating the concentration of water. No data were available on the density of sulphite liquor in the concentration and temperature range desired. Therefore, the density of sulphurous acid (11) was extrapolated to 130°C., and this value was used as the closest approximation. It was found that the relation obtained by taking into account the water concentration was slightly closer to the linear than that shown in Fig. 25. However, there was still a definite curvature greater than the experimental error. It is possible that hydration of the ions present, which would lower the (H_2O) still further, might account for the deviation from the linear relation. This would be impossible to calculate.

(c) A third explanation may be found in Fig. 26, in which the logarithm of the partial pressure of sulphur dioxide is plotted against the logarithm of the rate of delignification. It is observed that an excellent straight line is obtained. In other words, this relationship can be expressed mathematically by the equation:

$$1/t_{90\%} = KP^{n} \quad \ldots \ldots\ldots\ldots \quad (17)$$

where "K" and "n" are constants. This is the equation of the Freundlich adsorption isotherm and suggests the possibility of an adsorption process. The colloidal nature of lignin has frequently been pointed out, and if the concentration of the active cooking agent at the surface of the lignin particles was greater than in the body of the solution, such a relation would hold. That this relation has been found, does not, of course, prove that an adsorption process is involved, but the agreement

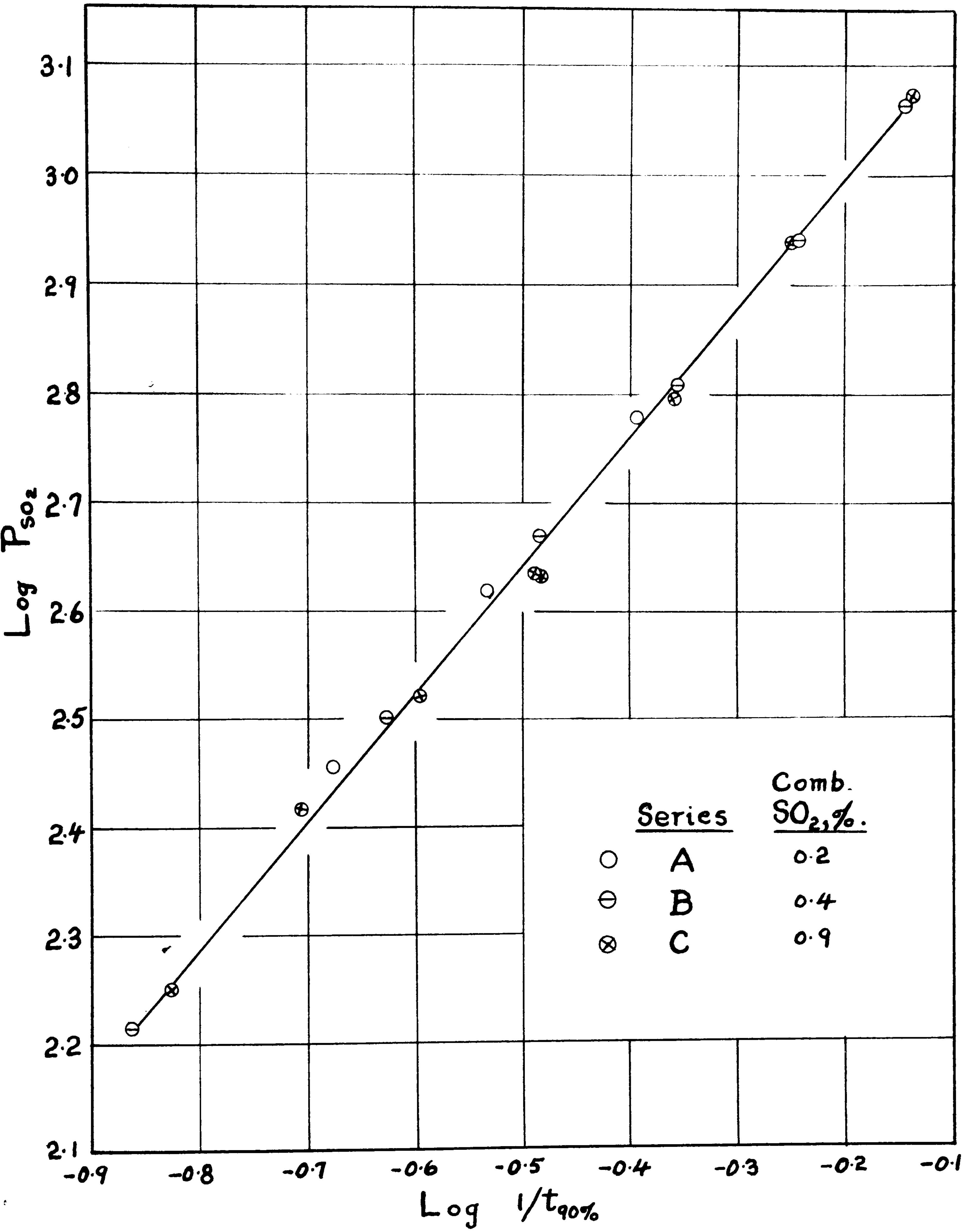


Fig. 26. The rate of delignification of spruce wood in calcium base sulphite liquor at 130°C as a function of the partial pressure of sulphur dioxide.

seems too close to be entirely fortuitous.

5. The Relation of the Hydrogen Ion Concentration to the Rate of Delignification

More information may be obtained from a study of the hydrogen ion concentration of the cooking liquors. It is realized that the presence of the wood may alter the pH of the liquor slightly, owing to the formation of lignin sulphonic acids. However, the very high liquor ratio used will minimize any such change during cooking, and the hydrogen ion concentration in these experiments can be considered approximately constant.

The actual hydrogen ion concentration of sulphite liquor at cooking temperatures cannot be measured directly. From vapor pressure and conductivity measurements, Gishler and Maass (23) have calculated the hydrogen ion concentration of calcium base sulphite liquors up to 90°C. They found that the logarithm of the hydrogen ion concentration plotted against the reciprocal of the absolute temperature gave a straight line. This made accurate extrapolation to 130°C. possible. A less accurate extrapolation for concentrations above 6% sulphur dioxide was necessary. In this way the actual pH of each liquor was calculated, where possible, and is given in Table 21.

In Fig. 27 the logarithm of the rate of delignification is plotted against the pH of the liquor at 130°C. for the three series of combined sulphur dioxide. It is observed that a straight line relation is obtained, and that the three series

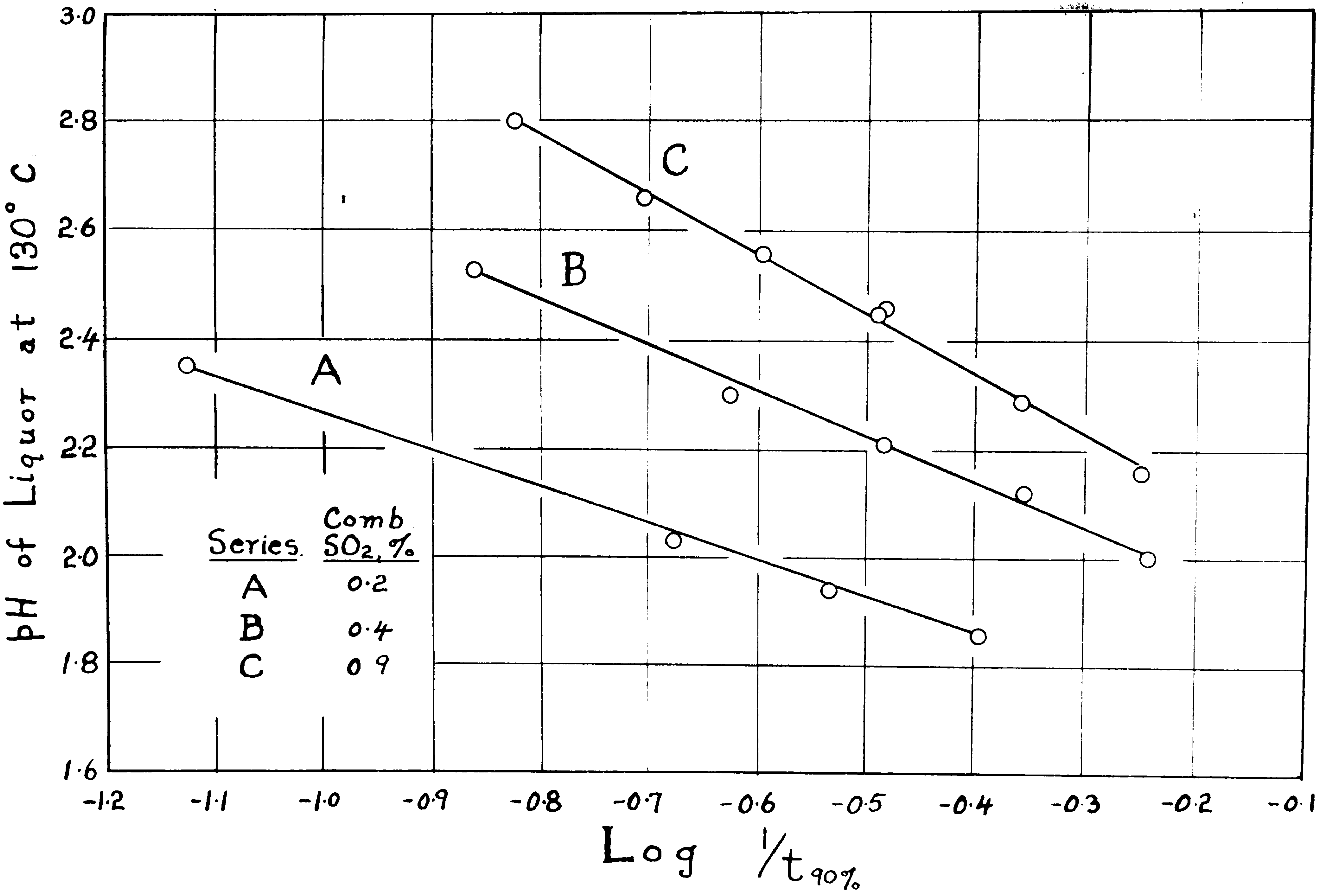


Fig. 27. The rate of delignification of spruce wood in calcium base sulphite liquor at 130°C. as a function of the hydrogen ion concentration

give three widely separated lines of almost the same slope. Obviously, the overall rate of delignification cannot be governed by the hydrogen ion concentration alone, or all of the points would fall on a single curve. The time required for the amount of delignification to increase from 80 to 90% and from 90 to 95% was also calculated for each run. When the logarithms of the reciprocals of these times were plotted against the pH of the liquor, straight line relations similar to those in Fig. 27 were obtained. Here again, three concentrations of combined sulphur dioxide gave three widely separated lines. This is conclusive evidence that even in the final stages of the reaction when sulphonation is presumably complete, the velocity of delignification is not determined by the hydrogen ion concentration alone, as claimed so frequently by Hägglund.

From the above results, it is evident that the addition of both lime and sulphur dioxide to a liquor in such proportions that the hydrogen ion concentration is not altered will greatly increase the rate of lignin removal. This can only be explained on the basis of the theory already outlined, that the cooking action is due to sulphurous acid or the hydrogen and bisulphite ions together, and not to either ion separately. The addition of lime, together with sufficient sulphur dioxide to keep the hydrogen ion concentration constant, increases the bisulphite ion concentration, and hence the rate of cooking. On the other hand, if the combined is held constant, an increase in the free sulphur dioxide increases the hydrogen ion concentration (lowers the pH, Fig. 27), and also increases the rate of cooking.

If the normal cooking reaction is stopped and the partly cooked wood replaced in buffer solutions, naturally the velocity of subsequent delignification will be determined by the hydrogen ion concentration of the buffer, as reported by Hägglund (29) and Yorston (78). However, the present work has shown that this cannot be interpreted as evidence that the rate of delignification in sulphite liquor is also governed by the hydrogen ion concentration alone, even in the final stages of cooking when the lignin is highly sulphonated.

B. The Effect of Composition of Magnesium Base Sulphite Liquor

The investigation of the rate of delignification of spruce wood in calcium base sulphite liquor showed that the combined sulphur dioxide could be varied over only a comparatively small range of concentration, without the danger of precipitation of calcium sulphite during cooking. Therefore, the rate of delignification of spruce wood in magnesium base sulphite liquor was investigated, since a much greater range of combined sulphur dioxide was possible. It was hoped that this would permit a more precise correlation of the composition variables with the rate of delignification, and in addition prove an interesting comparison with the calcium system in regard to both the rate of cooking and the yield of pulp.

The data for 26 runs are reported in Table 22, again arranged in order of increasing total sulphur dioxide in each series of combined. The initial concentration of combined sulphur dioxide was varied from 0.5 to 4.0%, and the total sulphur dioxide from 2 to 14%. The calculations were all made in the same manner as described in Part II,A for the calcium system. The correction for the sulphur dioxide lost to the vapor phase was calculated using the vapor pressures of calcium base liquor, since no data were available for the magnesium system. This was sufficiently accurate because the magnitude of the correction is small.

The yield of pulp for each run was plotted against the

TABLE 22

The Effect of Composition of Magnesium Base Sulphite Liquor on the Rate of Delignification of Spruce Wood and Yield of Pulp

Wood:- spruce meal, 40-100 mesh. Density 0.43. Extracted in Soxhlet 12 hr., alcohol-benzene (1:2). Lignin 27.5%, extracted wood basis.

Cooking:- Pyrex bombs, 130°C.

I	II	III	IV	V	VI	VII	VIII
Time in bath (uncorr.), hours	Comb. SO_2, %	Total SO_2 (uncorr.), %	Total SO_2 (corr.), %	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood
Series A Initial combined sulphur dioxide, 0.5%.							
Run No. 105. Average total sulphur dioxide, 2.15%.							
3.00	0.45	2.22	2.21	68.9	53.9	21.7	15.0
6.00	0.40	2.19	2.17	56.6	49.7	12.1	6.85
8.00	0.41	2.18	2.17	49.5	46.8	5.37	2.66
10.00	0.39	2.12	2.11	48.3	46.7	3.31	1.60
12.00	0.38	2.12	2.11	46.8	45.9	1.92	0.90
15.00	0.39	2.15	2.14	45.0	44.4	1.30	0.59
Average	0.40	2.16	2.15				
Run No. 104. Average total sulphur dioxide, 3.40%.							
2.00	0.42	3.48	3.46	67.2	52.3	22.1	14.9
3.50	0.39	3.40	3.37	55.6	48.8	12.2	6.78
4.50	0.38	3.44	3.41	51.1	47.7	6.74	3.44
5.50	0.38	3.43	3.39	48.2	46.4	3.70	1.78
7.00	0.38	3.40	3.37	46.4	45.5	1.92	0.89
Average	0.39	3.43	3.40				

TABLE 22 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 102. Average total sulphur dioxide, 4.70%.							
1.00	0.48	4.79	4.75	75.1	57.3	23.8	17.8
2.00	0.46	4.77	4.72	63.8	53.5	16.2	10.3
2.75	0.45	4.80	4.72	56.3	51.2	9.01	5.07
3.50	0.42	4.78	4.71	52.8	50.0	5.32	2.81
4.25	0.45	4.66	4.62	50.5	49.0	2.87	1.45
5.00	0.42	4.71	4.68	48.9	48.1	1.72	0.84
Average	0.45	4.75	4.70				
Run No. 103. Average total sulphur dioxide, 6.51%.							
0.75	0.47	6.49	6.48	75.6	56.8	24.9	18.8
1.50	0.46	6.57	6.54	64.6	53.0	17.9	11.6
2.25	0.45	6.54	6.47	53.5	49.3	7.88	4.21
2.75	0.44	6.63	6.55	51.6	49.2	4.58	2.36
3.25	0.44	6.58	6.52	50.2	48.8	2.83	1.42
4.00	0.41	6.55	6.47	48.2	47.5	1.38	0.67
Average	0.44	6.56	6.51				
Run No. 107. Average total sulphur dioxide, 8.63%.							
0.50	0.47	8.58	8.48	77.4	56.8	26.7	20.6
1.00	0.47	8.70	8.64	66.0	52.6	20.3	13.4
1.50	0.46	8.75	8.60	55.3	49.6	10.3	5.68
2.00	0.45	8.78	8.70	50.9	48.3	5.14	2.62
2.50	0.43	8.81	8.73	48.1	46.8	2.67	1.29
3.00	0.41	8.72	8.66	46.7	46.0	1.60	0.75
Average	0.45	8.72	8.63				
Series B Initial combined sulphur dioxide, 1.0%.							
Run No. 82. Average total sulphur dioxide, 2.44%.							
3.00	0.92	2.52	2.51	76.9	60.8	21.0	16.1
6.00	0.90	2.48	2.47	69.0	57.9	16.0	11.1
9.00	0.90	2.47	2.46	61.3	55.6	9.25	5.67
12.00	0.88	2.43	2.42	56.4	53.8	4.57	2.58
15.00	0.86	2.41	2.40	53.8	52.5	2.36	1.27
18.00	0.85	2.37	2.36	52.3	51.5	1.55	0.81
Average	0.88	2.45	2.44				

TABLE 22 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 81. Average total sulphur dioxide, 3.95%.							
1.50	1.01	4.04	4.01	78.9	62.0	21.5	16.9
3.00	0.98	3.98	3.96	69.2	58.6	15.3	10.6
4.50	1.00	3.98	3.96	59.9	55.2	7.90	4.74
5.50	1.00	4.02	4.00	56.8	54.3	4.48	2.54
6.50	0.94	3.90	3.87	54.8	53.0	3.27	1.79
8.00	0.94	3.92	3.90	52.3	51.7	1.14	0.60
Average	0.98	3.97	3.95				
Run No. 90 Average total sulphur dioxide, 5.01%.							
1.00	0.95	5.08	5.03	78.3	61.3	21.7	17.0
2.03	0.92	5.05	5.00	67.7	57.5	15.1	10.2
3.00	0.92	5.12	5.07	60.9	55.6	8.70	5.30
3.75	0.90	5.06	5.00	56.7	53.9	4.85	2.75
4.50	0.91	5.04	4.99	53.8	52.6	2.16	1.16
5.50	0.89	5.00	4.94	51.6	51.0	1.09	0.56
Average	0.92	5.06	5.01				
Run No. 87. Average total sulphur dioxide, 6.16%.							
1.00	0.97	6.32	6.27	76.9	60.9	20.6	16.0
2.00	0.92	6.18	6.12	63.9	56.2	12.1	7.70
3.00	0.92	6.22	6.18	55.2	52.7	4.43	2.45
3.75	0.89	6.22	6.15	53.2	52.0	2.24	1.19
4.50	0.89	6.16	6.06	51.5	51.0	1.04	0.53
5.50	0.89	6.20	6.15	50.1	49.7	0.69	0.35
Average	0.91	6.22	6.16				
Run No. 83. Average total sulphur dioxide, 7.76%.							
0.75	0.97	7.99	7.93	77.3	61.5	20.4	15.8
1.50	0.94	7.86	7.72	65.7	57.3	12.8	8.4
2.25	0.93	7.76	7.70	57.1	53.6	6.04	3.45
2.75	0.91	7.82	7.79	54.1	52.6	2.76	1.49
3.25	0.91	7.84	7.76	52.3	51.0	1.94	1.01
4.00	0.88	7.79	7.67	50.5	50.0	1.01	0.51
Average	0.92	7.84	7.76				

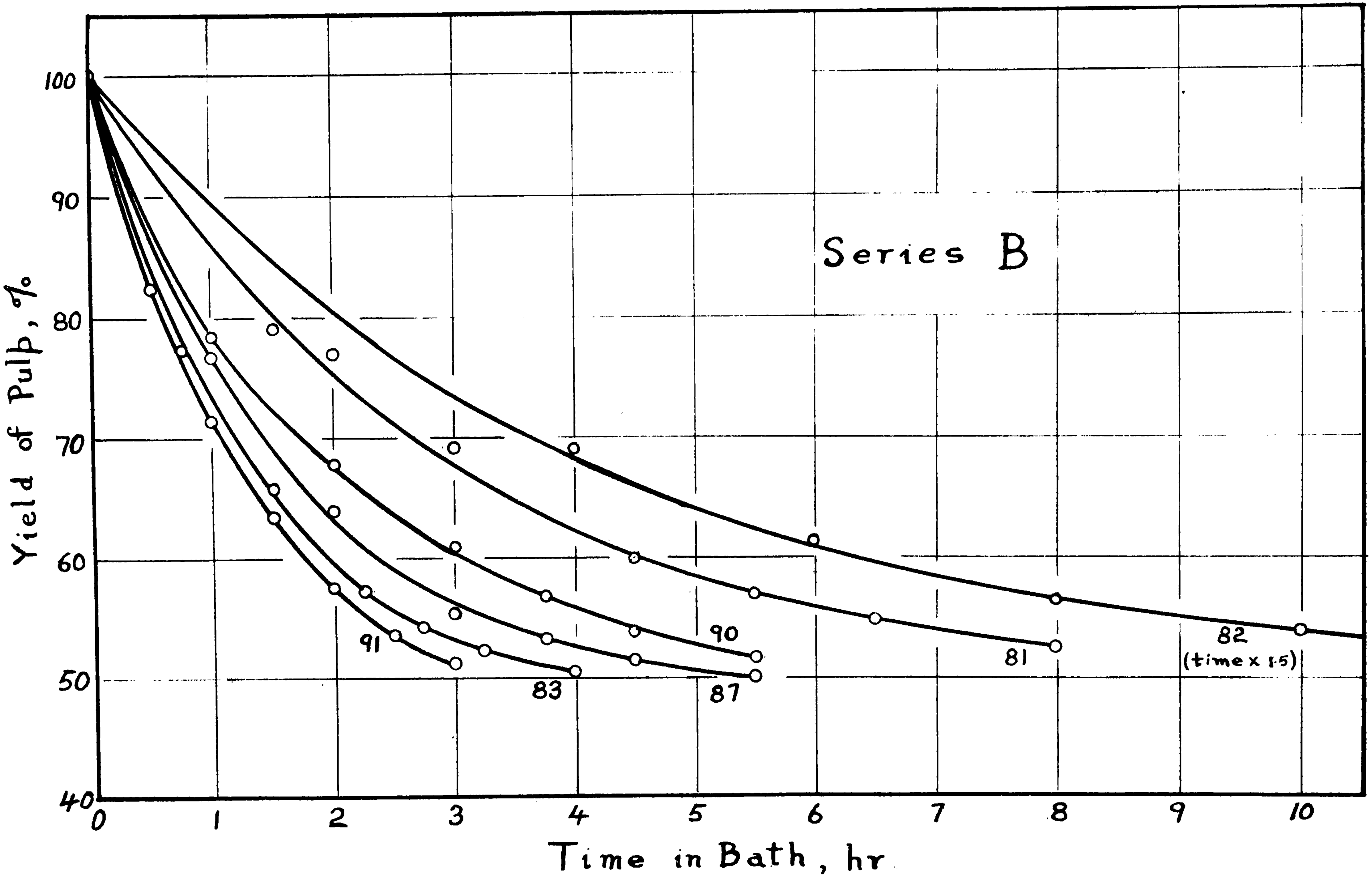


Fig. 28. The effect of the free sulphur dioxide concentration on the yield of pulp. Magnesium base sulphite liquor; average combined sulphur dioxide 0.92%; temperature 130°C.

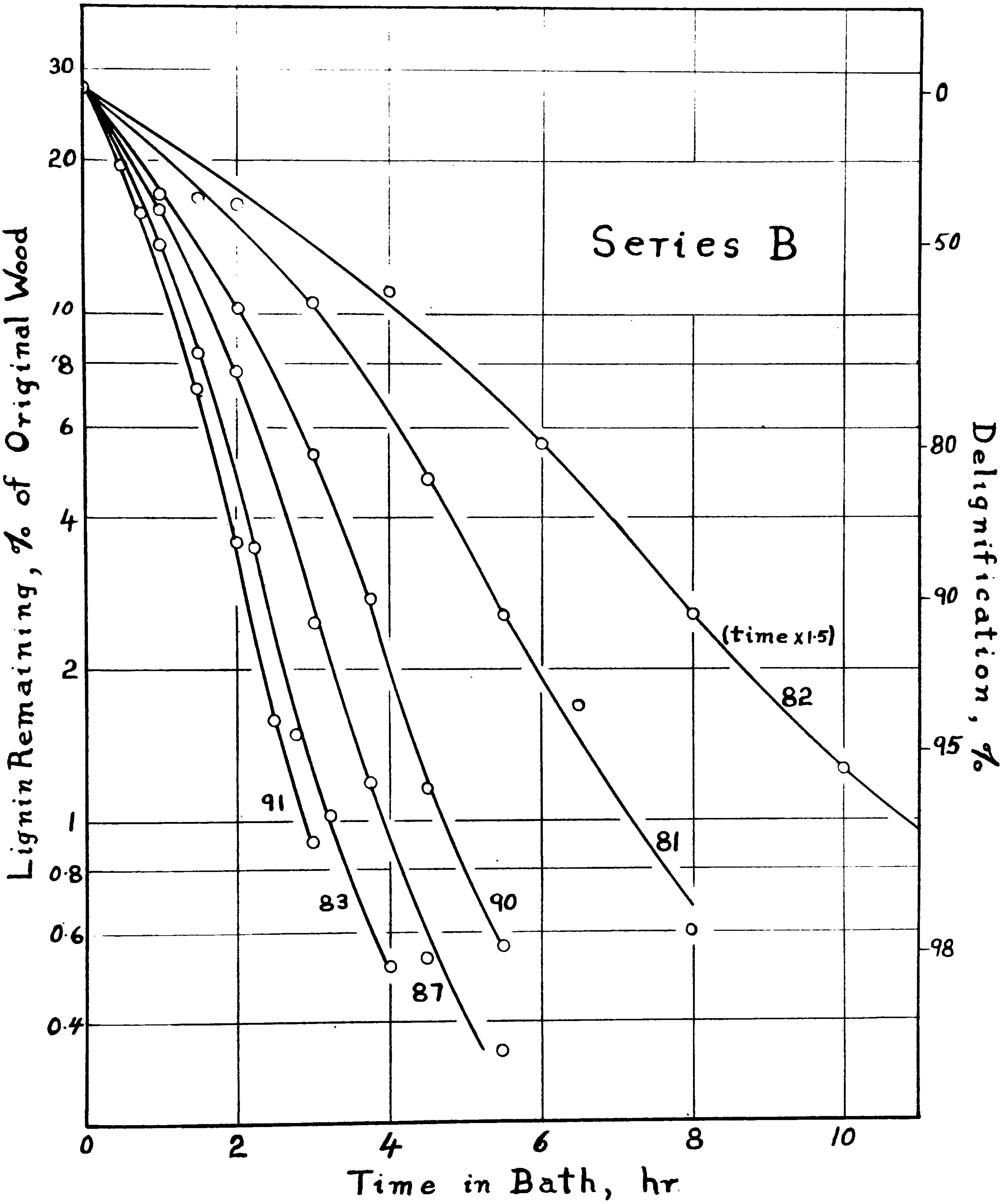


Fig. 29. The effect of the free sulphur dioxide concentration on the rate of delignification of spruce wood. Magnesium base sulphite liquor; average combined sulphur dioxide 0.92%; temperature 130°C.

TABLE 22 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 91.	Average total sulphur dioxide, 9.05%.						
0.50	0.96	9.08	9.02	82.5	63.0	23.6	19.5
1.00	0.93	9.12	9.03	71.4	57.8	19.1	13.6
1.50	0.92	9.14	9.01	63.3	56.2	11.3	7.14
2.00	0.91	9.18	9.12	57.6	54.0	6.16	3.55
2.50	0.90	9.16	9.07	53.6	52.0	2.96	1.58
3.00	0.88	9.18	9.03	51.3	50.4	1.75	0.90
Average	0.92	9.14	9.05				
Series C	Initial combined sulphur dioxide, 2.0%.						
Run No. 96.	Average total sulphur dioxide, 4.62%.						
2.00	1.96	4.74	4.71	83.0	66.6	19.8	16.4
4.00	1.96	4.74	4.72	72.2	61.5	14.8	10.7
6.00	1.94	4.66	4.61	65.1	59.0	9.43	6.14
7.50	1.92	4.62	4.60	60.9	56.8	6.77	4.12
9.00	1.91	4.62	4.57	58.8	56.4	4.02	2.36
11.00	1.88	4.58	4.52	56.0	54.5	2.73	1.53
Average	1.93	4.66	4.62				
Run No. 92.	Average total sulphur dioxide, 5.64%.						
1.50	1.95	5.74	5.69	81.0	65.3	19.4	15.7
3.00	1.95	5.78	5.73	69.3	60.4	12.8	8.87
4.50	1.91	5.71	5.67	62.0	58.4	5.74	3.55
5.50	1.90	5.64	5.62	58.1	56.4	3.00	1.74
6.50	1.90	5.68	5.62	56.9	55.6	2.28	1.30
7.50	1.90	5.55	5.50	54.8	54.3	0.90	0.50
Average	1.92	5.68	5.64				
Run No. 98.	Average total sulphur dioxide, 7.03%.						
1.00	2.04	7.08	7.04	81.0	64.1	20.9	16.9
2.00	1.97	7.04	6.97	69.0	59.4	13.9	9.59
2.75	1.90	7.04	6.94	61.7	56.6	8.23	5.08
3.50	2.00	7.18	7.13	58.0	55.1	5.06	2.93
4.25	1.97	7.12	7.07	55.4	54.2	2.24	1.24
5.00	1.94	7.06	7.01	53.4	52.6	1.51	0.81
Average	1.97	7.09	7.03				

TABLE 22 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 84. Average total sulphur dioxide, 8.59%.							
0.75	1.95	8.77	8.73	82.0	64.4	21.5	17.6
1.75	1.91	8.78	8.71	67.9	60.7	10.6	7.19
2.50	1.89	8.54	8.52	60.9	58.0	4.82	2.93
3.25	1.90	8.62	8.55	56.0	54.8	2.22	1.24
4.00	1.86	8.50	8.44	53.8	53.3	0.93	0.50
Average	1.90	8.64	8.59				
Run No. 94. Average total sulphur dioxide, 10.36%.							
0.50	1.98	10.30	10.23	85.7	65.6	23.5	20.1
1.00	1.96	10.56	10.47	74.5	61.1	18.0	13.4
1.50	1.94	10.56	10.46	66.7	59.7	10.5	7.00
2.00	1.94	10.46	10.41	60.3	57.1	5.33	3.21
2.50	1.90	10.36	10.29	56.1	55.0	2.03	1.14
3.00	1.92	10.36	10.29	55.2	54.6	1.14	0.63
Average	1.94	10.43	10.36				
Series D Initial combined sulphur dioxide, 3.0%.							
Run No. 100. Average total sulphur dioxide, 6.38%.							
3.00	2.97	6.54	6.51	78.8	66.7	15.3	12.1
6.00	2.92	6.47	6.45	68.0	61.3	9.78	6.65
8.00	2.90	6.48	6.43	63.7	59.8	6.08	3.87
10.00	2.88	6.45	6.40	60.2	58.0	3.63	2.19
12.00	2.85	6.35	6.31	57.7	56.6	1.97	1.14
15.00	2.79	6.22	6.20	55.0	54.5	0.89	0.51
Average	2.89	6.42	6.38				
Run No. 95. Average total sulphur dioxide, 7.52%.							
1.00	2.91	7.60	7.56	87.7	69.0	21.3	18.7
2.00	2.91	7.60	7.54	77.0	63.9	17.0	13.1
3.00	2.92	7.64	7.58	70.5	62.0	12.1	8.52
4.00	2.88	7.58	7.52	65.3	60.0	8.19	5.35
5.00	2.86	7.56	7.49	61.1	58.1	4.95	3.02
6.00	2.86	7.50	7.44	57.6	55.5	3.51	2.02
Average	2.89	7.58	7.52				

TABLE 22 (continued)

Run No. 97. Average total sulphur dioxide, 9.10%.

I	II	III	IV	V	VI	VII	VIII
1.00	2.95	9.18	9.15	82.1	67.3	18.0	14.8
2.00	2.93	9.12	9.10	70.9	62.0	12.6	8.93
2.75	2.94	9.18	9.15	64.5	59.9	7.07	4.56
3.50	2.92	9.10	9.07	59.8	57.4	3.98	2.38
4.25	2.92	9.08	9.03	57.2	56.1	1.85	1.06
Average	2.93	9.13	9.10				

Run No. 99. Average total sulphur dioxide, 10.49%.

I	II	III	IV	V	VI	VII	VIII
0.75	2.91	10.60	10.54	82.6	65.4	20.8	17.2
1.50	2.90	10.66	10.58	70.7	60.9	13.9	9.82
2.00	--	-	-	65.0	58.8	9.53	6.20
2.50	2.87	10.58	10.49	61.4	58.6	4.60	2.82
3.00	2.83	10.54	10.47	57.9	56.1	3.17	1.83
3.75	2.78	10.44	10.35	54.3	53.6	1.34	0.73
Average	2.86	10.56	10.49				

Run No. 101. Average total sulphur dioxide, 12.56%.

I	II	III	IV	V	VI	VII	VIII
0.50	3.00	12.72	12.64	89.4	69.0	22.8	20.4
1.00	2.96	12.66	12.58	75.5	62.8	16.8	12.7
1.53	2.95	12.74	12.59	66.4	59.9	9.77	6.49
2.00	2.92	12.64	12.49	61.4	58.2	5.16	3.17
2.50	2.92	12.68	12.58	57.4	55.9	2.68	1.54
3.00	2.86	12.58	12.45	55.0	54.1	1.69	0.93
Average	2.93	12.67	12.56				

Series E Initial combined sulphur dioxide, 4.0%.

Run No. 110. Average total sulphur dioxide, 8.35%.

I	II	III	IV	V	VI	VII	VIII
3.00	3.98	8.72	8.67	79.0	65.5	17.1	13.5
6.00	3.90	8.56	8.53	67.3	60.4	10.3	6.93
9.00	3.80	8.34	8.32	59.5	57.3	3.75	2.23
12.00	3.71	8.20	8.15	55.3	54.5	1.54	0.85
15.00	3.69	8.10	8.07	52.9	52.5	0.80	0.42
Average	3.82	8.38	8.35				

TABLE 22 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 109. Average total sulphur dioxide, 10.00%.							
1.50	4.00	10.20	10.15	79.4	64.1	19.3	15.3
3.00	3.97	10.20	10.16	67.0	59.5	11.2	7.50
4.50	3.95	10.12	10.01	59.3	56.4	4.90	2.90
5.50	3.87	10.00	9.93	55.8	54.3	2.69	1.50
6.50	3.84	9.92	9.87	54.8	53.8	1.73	0.95
8.00	3.80	9.89	9.85	52.0	51.5	0.95	0.49
Average	3.91	10.05	10.00				
Run No. 106. Average total sulphur dioxide, 11.62%.							
1.00	3.96	11.74	11.72	80.1	64.1	20.0	16.0
2.00	3.96	11.80	11.73	68.8	61.1	11.2	7.71
2.75	3.94	11.76	11.69	62.6	58.2	7.09	4.44
3.50	3.92	11.68	11.56	58.7	56.5	3.68	2.16
4.25	3.90	11.62	11.55	54.8	53.9	1.74	0.94
5.00	3.83	11.54	11.47	52.8	52.3	1.00	0.53
Average	3.92	11.69	11.62				
Run No. 113. Average total sulphur dioxide, 12.47%.							
0.75	3.88	12.56	12.44	84.3	66.3	21.4	18.0
1.50	3.88	12.72	12.60	71.3	61.6	13.6	9.70
2.25	3.87	12.68	12.52	63.2	58.9	6.84	4.32
2.75	3.83	12.60	12.46	60.2	57.4	4.67	2.81
3.25	3.80	12.52	12.42	56.6	54.9	3.05	1.73
4.03	3.77	12.40	12.36	52.4	51.7	1.37	0.72
Average	3.84	12.58	12.47				
Run No. 112. Average total sulphur dioxide, 14.21%.							
0.50	3.95	14.34	14.24	88.1	67.2	23.7	20.9
1.00	3.90	14.34	14.29	74.9	62.2	17.0	12.7
1.50	3.86	14.40	14.28	67.5	59.7	11.5	7.78
2.00	3.83	14.32	14.13	61.4	56.9	7.34	4.51
2.50	3.81	14.32	14.22	56.5	54.2	4.01	2.26
3.00	3.79	14.24	14.07	54.3	52.9	2.58	1.40
Average	3.86	14.33	14.21				

Table 23

SUMMARY OF THE EFFECT OF COMPOSITION OF MAGNESIUM BASE SULPHITE LIQUOR ON THE DELIGNIFICATION OF SPRUCE WOOD AT 130°C.

Series No.	Run No.	Average final concentration of sulphur dioxide (corrected)					80% delignification		90% delignification		95% delignification		Time to 90% delignification (corrected), hours = $t_{90\%}$	Rate of delignification = $1/t_{90\%}$
		Combined, %	Total, %	Free (total-comb.), %	Total-1.5 x comb., %	Excess (total-2 x comb.), %	Time (uncorr.), hours	Yield of pulp, %	Time (uncorr.), hours	Yield of pulp, %	Time (uncorr.), hours	Yield of pulp, %		
A	105	0.40	2.15	1.75	1.55	1.35	6.40	54.3	8.28	50.3	10.25	48.0	8.06	0.124
	104	0.39	3.40	3.01	2.81	2.62	3.82	54.0	4.83	50.3	5.98	47.8	4.61	0.217
	102	0.45	4.70	4.25	4.03	3.80	2.70	56.8	3.53	52.7	4.32	50.2	3.31	0.302
	103	0.44	6.51	6.07	5.85	5.63	2.05	57.0	2.63	52.4	3.26	50.2	2.41	0.415
	107	0.45	8.63	8.18	7.95	7.73	1.57	55.3	2.00	51.0	2.45	48.4	1.78	0.562
	Av.	0.43						55.5		51.3		48.9		
B	82	0.88	2.44	1.56	1.12	0.68	9.13	61.0	11.78	56.6	14.60	54.0	11.56	0.0865
	81	0.98	3.95	2.97	2.48	1.99	4.25	60.8	5.38	57.0	6.65	54.2	5.16	0.194
	90	0.92	5.01	4.09	3.63	3.17	2.96	60.8	3.75	56.7	4.34	54.3	3.53	0.283
	87	0.91	6.16	5.25	4.80	4.34	2.37	60.2	3.02	55.6	3.60	53.5	2.80	0.357
	83	0.92	7.76	6.84	6.38	5.92	1.89	60.6	2.40	56.3	2.88	53.5	2.18	0.458
	91	0.92	9.05	8.13	7.67	7.21	1.70	60.8	2.12	56.3	2.62	52.9	1.90	0.527
	Av.	0.92						60.7		56.4		53.7		
C	96	1.93	4.62	2.69	1.72	0.76	6.45	63.8	8.60	59.0	10.75	56.2	8.38	0.119
	92	1.92	5.64	3.72	2.76	1.80	3.85	64.7	4.83	60.6	5.86	57.8	4.61	0.217
	98	1.97	7.03	5.06	4.07	3.09	2.74	62.7	3.47	58.2	4.15	55.8	3.25	0.308
	84	1.90	8.59	6.69	5.74	4.79	2.00	65.5	2.56	60.6	3.15	56.5	2.34	0.427
	94	1.94	10.36	8.42	7.45	6.48	1.67	64.3	2.08	59.3	2.41	56.7	1.86	0.538
	Av.	1.93						64.2		59.5		56.6		
D	100	2.89	6.38	3.49	2.04	0.60	6.70	66.3	9.20	61.5	11.42	58.2	8.98	0.111
	95	2.89	7.52	4.63	3.18	1.74	3.94	65.7	5.24	60.2	6.75	56.7	5.02	0.199
	97	2.93	9.10	6.17	4.70	3.24	2.58	65.9	3.33	60.8	4.01	58.0	3.11	0.322
	99	2.86	10.49	7.63	6.20	4.77	2.07	64.7	2.62	60.4	3.13	57.3	2.40	0.417
	101	2.93	12.56	9.63	8.16	6.70	1.64	65.4	2.08	60.7	2.61	56.8	1.86	0.538
	Av.	2.90						65.6		60.7		57.4		
E	110	3.82	8.35	4.53	2.62	0.71	6.66	65.2	8.49	60.7	10.41	57.2	8.27	0.121
	109	3.91	10.00	6.09	4.13	2.18	3.52	64.0	4.58	59.1	5.70	55.8	4.36	0.230
	106	3.92	11.62	7.70	5.74	3.78	2.49	64.5	3.25	59.5	3.90	56.3	3.03	0.330
	113	3.84	12.47	8.63	6.71	4.79	2.06	65.0	2.76	59.7	3.50	55.0	2.54	0.394
	112	3.86	14.21	10.35	8.42	6.49	1.82	63.1	2.34	58.1	3.02	54.2	2.12	0.472
	Av.	3.87						64.4		59.4		55.7		

J.M.C 8/10/38.

observed time of cooking, e.g., Series B, Fig. 28. The lignin remaining, as percent of the original wood, was also plotted on a logarithmic scale against the observed time of cooking, e.g., Series B, Fig. 29. The uncorrected times to 80, 90 and 95% delignification for each run were read from the delignification curves, and the yields of pulp at the corresponding times were read from the yield curves.

A complete summary of the experimental data is given in Table 23. The rate of delignification is again taken as $1/t_{90\%}$, where "$t_{90\%}$" is the corrected time to 90% delignification, obtained by subtracting 0.22 hours from the observed time, as previously explained. Since the investigation of the reaction in both magnesium and calcium base liquor was carried out under identical experimental conditions and with the same sample of wood, the results in the two cases are strictly comparable. However, interpretation of the results for the delignification of wood in magnesium base sulphite liquor is handicapped by the fact that no equilibria data exists as yet, and the actual ion concentrations at different temperatures cannot be calculated. Vapor pressure and conductivity measurements on the system magnesium oxide — sulphur dioxide — water are being made in this laboratory at the time of writing by King (44), but sufficient information is not yet available.

1. The Effect of Liquor Composition on the Yield of Pulp

Table 23 shows that when cooking with magnesium base sulphite liquor, the yield of pulp at a given lignin content is practically independent of the free sulphur dioxide when the combined is constant, as was also found with the calcium base cooks. In Fig. 30, the average yield of pulp for each series of combined, taken at 80, 90 and 95% delignification, is plotted against the average combined sulphur dioxide. The dotted curves show the same data for the calcium base cooks taken from Fig. 20 for comparison.

It is observed that the yield of pulp from magnesium base cooks increases rapidly at first and then more slowly, reaching a maximum value at a concentration of about 3% combined sulphur dioxide, beyond which it drops slightly. Somewhat lower yields are obtained from magnesium than from calcium base cooks at low concentrations of combined sulphur dioxide, but somewhat higher yields are obtained at concentrations above 1% combined.

The effect of liquor composition on the yield of pulp can be explained by the fact that the rate of degredation of cellulose at a given temperature depends chiefly on the hydrogen ion concentration of the liquor and the length of the cook. That is, the yield of pulp at a given lignin content depends on the rate of delignification as well as the acidity of the liquor. For a constant free sulphur dioxide, an increase in the combined decreases the hydrogen ion concentration of the liquor, which decreases the rate of degredation of cellulose and increases the yield of pulp. However, in the case of magnesium base cooks, it will be shown that an increase in the combined sulphur dioxide at constant free, also decreases the rate of delignification, which lengthens the time required for cooking and so reduces the yield of pulp. It is these two opposing actions which explain the maximum in the yield vs. combined sulphur dioxide curves for magnesium base cooks (Fig. 30).

In the case of calcium base cooks on the other hand, it was shown that the rate of delignification is practically independent of the combined sulphur dioxide when the free is constant, at least over the range of concentration studied. Hence, no maximum in the yield curves for calcium base cooks is apparent. In both magnesium and calcium base cooks, the rate of delignification is approximately proportional to the free sulphur dioxide when the combined is constant. Therefore, the increase in the hydrogen ion concentration due to an increase in the free sulphur dioxide is balanced by a decrease in the time required for cooking. This explains the approximate constancy of yield at a given combined sulphur dioxide for both magnesium and calcium base cooks.

The difference in magnitude of the yield of pulp from magnesium, as compared with calcium base cooks is not very great. According to Hiller (40), the waste liquor from magnesium base cooks has a higher pH than the waste liquor from calcium base cooks. This would explain the improved yield of pulp, which in any case is not large enough to be of practical importance.

2. The Effect of Liquor Composition on the Shape of the Delignification Curve

To compare the shape of the delignification curves in

Fig. 29, the corrected time of cooking for each separate bomb was multiplied by the arbitrary factor $6/t_{90\%}$ to make the curves coincident at the point corresponding to 90% delignification. The data were then plotted according to the relation "log L vs. time" and are shown in Fig. 31. As in the case of the calcium base cooks, all the points fall close to the same curve irrespective of the liquor composition. That is, an increase in the concentration of sulphur dioxide does not alter the shape of the delignification curve. It is observed that the curve is again a reversed S-shape, deviating considerably from the straight (dotted) line or first order relationship.

The same data are also shown in Fig. 31, plotted according to the relation "$L^{1/3}$ vs. time". The result is exactly the same as in the case of the calcium base cooks (Fig. 22). A much better straight line is obtained than is given by the first order relation. After the reaction is 95% complete, the rate falls off in the same manner as observed before, and the best straight line again extrapolates to a lignin value about 1% less than the lignin content of the original wood. Nevertheless, it is interesting that this relationship should hold in every case so much better than the first order relation for at least 95% of the reaction.

3. The Relation of the Free Sulphur Dioxide to the Rate of Delignification

The average concentration of free sulphur dioxide for each run is listed in Table 23 and plotted against the rate of

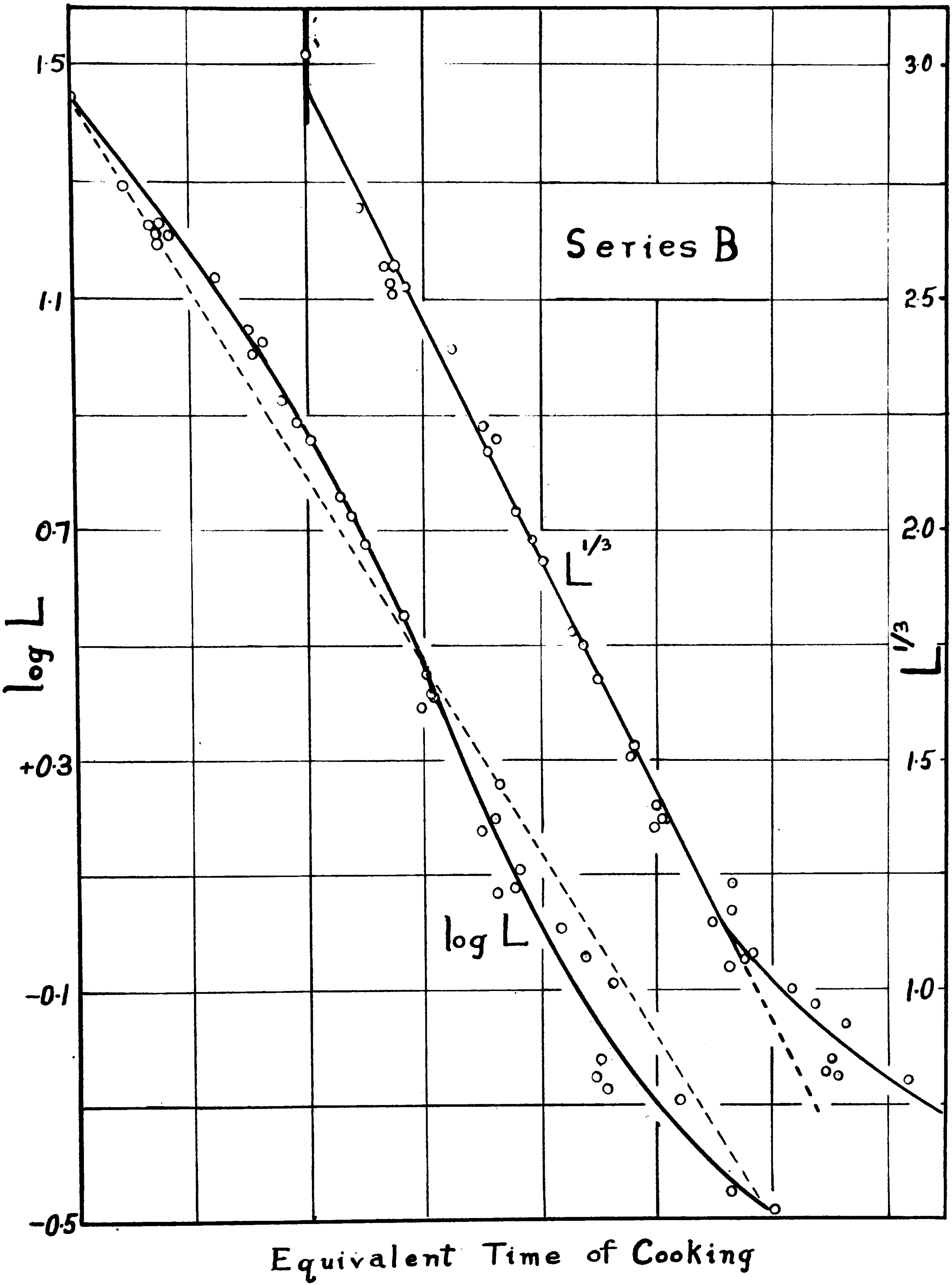


Fig. 31. The effect of the free sulphur dioxide concentration on the shape of the delignification curve. Magnesium base sulphite liquor; average combined sulphur dioxide 0.92%; temperature 130°C.

delignification ($1/t_{90\%}$) in Fig. 32. The dotted curve is for Series C of the calcium base cooks, taken from Fig. 23 for comparison.

An inspection of Fig. 32 brings a number of interesting facts to light. It is observed that the five series of combined sulphur dioxide give widely separated curves, none of which extrapolate to zero rate at zero concentration of free sulphur dioxide. Therefore, the rate of delignification of spruce wood in magnesium base sulphite liquor is decidedly not governed by the concentration of free sulphur dioxide alone, but decreases with increasing concentration of combined. This is contrary to the results obtained with calcium base cooks. However, all the curves in Fig. 32 are concave upward, similar to those obtained with calcium base cooks, indicating that the rate of reaction does not increase as rapidly at the higher concentrations of free sulphur dioxide.

The rate of delignification for each series was also plotted against the total -1.5 x combined sulphur dioxide, and against the total -2 x combined, as in the case of the calcium base cooks. The experimental data did not show any agreement with either relation. This can be made clearer in the following manner. The concentration of free sulphur dioxide for each series of combined, at the points corresponding to zero rate of delignification, was obtained by extrapolating the curves in Fig. 32. These values are listed in Table 24, together with the total sulphur dioxide (free + combined), and the ratio of the total to the combined sulphur dioxide, all at zero rate of delignification.

TABLE 24

The Composition of Magnesium Base Sulphite Liquor at Points Corresponding to Zero Rate of Delignification

Average combined SO_2, %	Free SO_2, %	Total SO_2, %	$\frac{\text{Total } SO_2}{\text{Comb. } SO_2} = n$
0.43	0.10	0.53	1.23
0.92	0.45	1.37	1.49
1.93	1.20	3.13	1.62
2.90	2.10	5.00	1.73
3.87	2.95	6.82	1.76

Now, if the rate of delignification were related to the liquor composition in any simple manner such as,

$$1/t_{90\%} = K\,(\text{total } SO_2 - n \text{ comb. } SO_2) \quad \ldots\ldots\ldots \quad (18)$$

where "K" and "n" are constants, then the ratio of the total to the combined sulphur dioxide at zero rate of delignification would also be constant and equal to "n" . If the free or the excess sulphur dioxide determined the rate of delignification, "n" would equal 1.0, or 2.0 respectively. The last column of Table 24 shows that this is not the case; "n" increases rapidly at first and then more slowly with increasing concentration of combined sulphur dioxide. Consequently, no relation of this type will fit the experimental results, and the only conclusion is that the concentration of the active cooking agent in magnesium base sulphite liquor is not proportional to the analytical composition. Before any quantitative relation can be established between the rate of delignification and the liquor composition, it will be necessary to have equilibria data on the magnesium system, which will enable the calculation of actual ion concentrations at cooking temperatures, as in the case of the calcium system.

The ratios of the total to the combined sulphur dioxide at zero rate of delignification, obtained by extrapolation and listed in Table 24, require further explanation. Since these ratios are greater than 1.0, it would appear that no delignification would occur if wood were cooked in solutions of neutral magnesium monosulphite. This is extremely ? kc unlightly since Aronovsky and Gortner (2) have shown that wood can be delignified in concentrated neutral sodium sulphite solutions at 170 to 186°C. However, Yorston (74) cooked wood in sodium sulphite solutions at 130°C. and found that only about one third of the lignin could be removed. It is, therefore, not unreasonable that an infinitely long time would be required to remove 90% of the lignin at 130°C. in solutions of magnesium sulphite, or even mixtures of magnesium sulphite and bisulphite. Since the time to 90% delignification has been taken as a measure of the rate of reaction in the present work, it is believed that the extrapolated concentrations in Table 24 closely approximate the truth. However, even if the curves in Fig. 32 do actually bend downward at low concentrations of free sulphur dioxide, it is only their relative positions with which we are concerned, and the statement made regarding the inadequacy of Equation (18) still holds.

It was shown in Part II, A, that the rate of delignification of spruce wood in calcium base sulphite liquor is practically independent of the concentration of combined sulphur dioxide when the free is constant, which is contrary to the results obtained with magnesium base cooks. This may be due to inherent differences in the two liquors, or the fact that only a comparatively small variation in the combined sulphur dioxide is possible in the calcium base cooks. Actually, Fig. 23 does show a small change in the rate of delignification with the combined sulphur dioxide at high concentrations of free, for calcium base cooks, but this variation disappears when the rate is plotted against the partial pressure of sulphur dioxide (Fig. 25). This point cannot be cleared up until the partial pressures of sulphur dioxide for magnesium base liquors are available.

Consider, now, the absolute velocities of delignification in magnesium base liquor (Series B), as compared with calcium base liquor (Series C') of the same concentration of combined sulphur dioxide. Fig. 32 shows that the reaction is noticeably more rapid in magnesium base liquor than in calcium base liquor of the same concentration. This fact has been reported before, and Berndt (7) suggests that the magnesium salts of lignin sulphonic acids may be more soluble than the corresponding calcium salts.

Yorston (77) found that jack pine wood cooked more rapidly in magnesium base liquor than in calcium, and more rapidly in sodium base liquor than in magnesium. It is interesting to note that this is the same order as that found for the pretreating effect of the respective cations in neutral salt solutions, which is reported in Part I, B, viz:

(a) The order of the rate of delignification in sulphite liquors:

$$Ca < Mg < Na$$

(b) The order of the severity of the pretreating effect in neutral salt solutions:

$$Ca > Mg > Na$$

This suggests that the difference in the rates of delignification in the three sulphite liquors might be related to the difference in the retarding action of the metal cations observed in pretreatment. If this were true, we would expect the delignification of wood in ammonium base sulphite liquor to be considerably slower than in calcium base liquor, because of the severe pretreating effect observed with neutral ammonium salt solutions. No data on these rates of delignification are available under comparable conditions, but wood has been successfully pulped in ammonium base sulphite liquor.

Since it has never been shown that the retarding action of various ions observed in pretreatment is actually present in a normal sulphite cook of untreated wood, it is perhaps more logical to look elsewhere for an explanation of the difference in the rate of delignification in different alkali base sulphite liquors. Considerable evidence was presented in Part II, A, which indicates that the rate of delignification of spruce wood in calcium base sulphite liquor is determined by the concentration of sulphurous acid or the product of the concentrations of the hydrogen and bisulphite ions. A comparison of the rates of delignification must, therefore, be made on the basis of the true ionic concentrations at cooking temperatures, rather than on the analytically determined concentrations.

It is certain that the hydrogen and bisulphite ion concentrations of magnesium base sulphite liquor differ from those of calcium base liquor of the same mole percent composition. Hence, it is possible that the increased rate of reaction in magnesium base liquor is not due to any specific effect of the metal cation itself, but is due to different equilibria conditions prevailing in the two liquors. As soon as the equilibria data on the magnesium system are available, it should be possible to settle these points. From a practical point of view, the difference in the rate of pulping in the two liquors is not of any commercial importance. The great advantage of magnesium base liquor is that the danger of precipitation, with consequent cooking difficulties, and "liming-up" of digesters is avoided. Better quality of pulp has also been claimed (40).

4. The Relation of the Combined Sulphur Dioxide to the Rate of Delignification

To obtain a clearer picture of the effect of the combined sulphur dioxide on the rate of delignification in magnesium base sulphite liquor, points were picked from the curves in Fig. 32 at constant concentrations of free sulphur dioxide, and replotted against the combined. The result is shown in Fig. 33, where all extrapolated points are joined by dotted lines.

It is observed that a symmetric family of curves is obtained, corresponding to different concentrations of free sulphur dioxide. These curves would all be perpendicular straight lines, if the rate of delignification were determined by the free sulphur dioxide alone. At low combined and high free sulphur dioxide, the rate of reaction does not vary greatly with the combined. However, at about 2% combined, the curves all bend sharply in a direction which indicates a marked decrease in the rate of cooking.

In Fig. 33, a line has been drawn through the points where the concentrations of free and combined sulphur dioxide are equal, i.e., where the composition of the liquor corresponds to magnesium bisulphite containing no excess sulphurous acid. The position and slope of this line shows that the rate of pulping in pure magnesium bisulphite solutions, although small, is appreciable, and increases slowly in an approximately linear manner with increasing concentration of magnesium bisulphite.

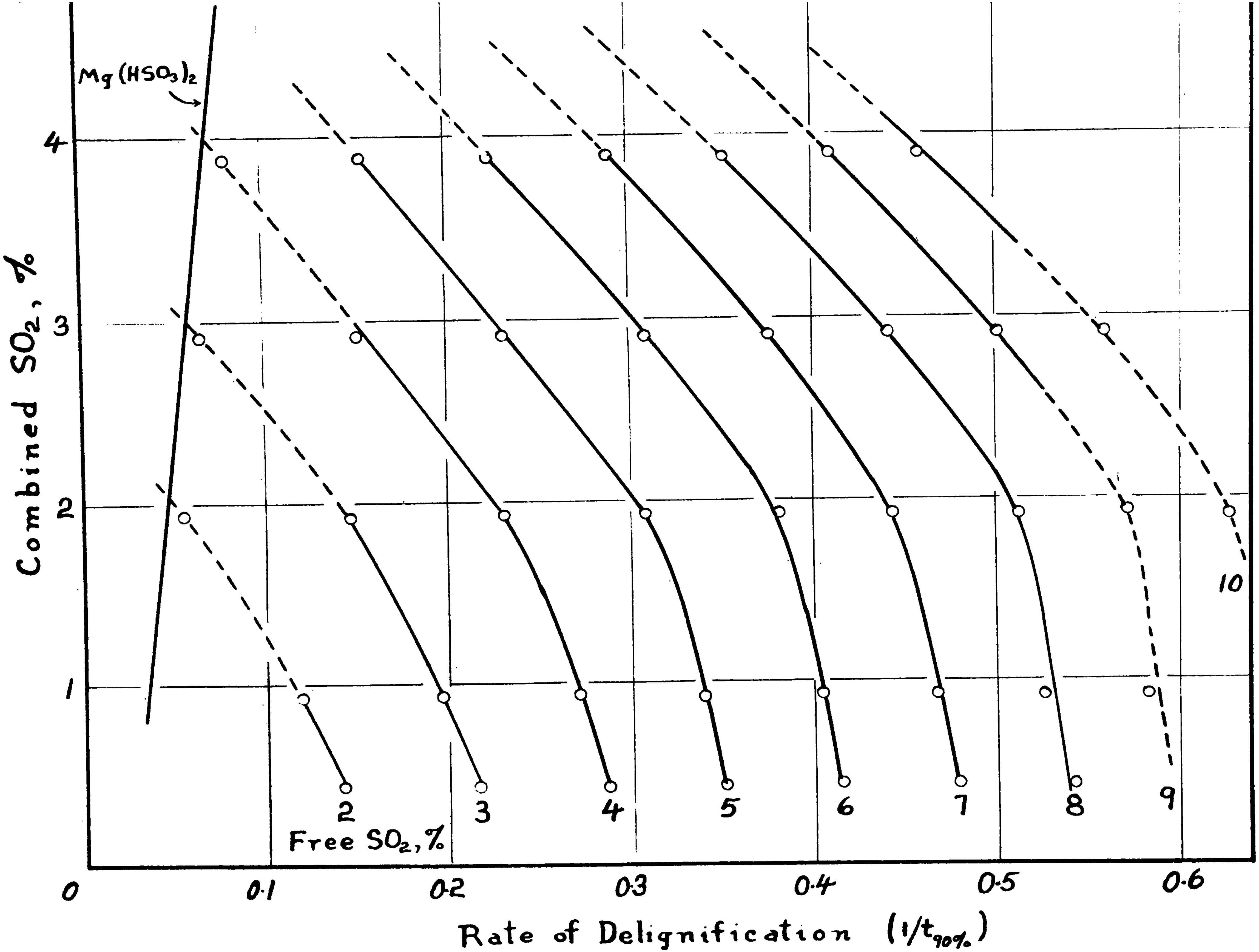


Fig. 33. The rate of delignification of spruce wood in magnesium base sulphite liquor at 130°C. as a function of the combined sulphur dioxide concentration.

It is impossible at the present time to offer any sound explanation for this effect of the combined sulphur dioxide on the rate of delignification. However, it is hoped that interpretation of the data presented will be facilitated when the actual concentrations of the hydrogen and bisulphite ions are known for all compositions of magnesium base sulphite liquor at cooking temperatures. This information should assist greatly in elucidating the mechanism of the delignification reaction.

From the above investigation of the cooking of spruce wood in magnesium base sulphite liquor, it is clear that the concentration of combined sulphur dioxide has an important effect on both the yield of pulp and the rate of delignification. There appears to be an optimum liquor concentration for cooking of about 1.5% combined sulphur dioxide. Below this value the yield of pulp shows a marked decrease, and above this value the rate of delignification is abnormally low. This concentration of combined sulphur dioxide is not feasible with a calcium base liquor because of solubility restrictions.

C. The Effect of Temperature

The investigation of the effect of temperature on the rate of delignification of spruce wood and yield of pulp was carried out in calcium base sulphite liquor. A high concentration of free sulphur dioxide was used, so that the reaction would be completed in a measureable time at the lower temperatures. Cooks were made at 50, 70, 90, 110 and 130°C. and the results are reported in Table 25.

1. The Effect of Temperature on the Yield of Pulp

Since pulp yields must be compared at the same lignin content, the effect of temperature on yield can be most clearly shown by plotting the yield of pulp against the percent lignin removed for each cook. This has been done in Fig. 34, and it is observed that the yield of pulp at any given lignin content decreases with increase in the cooking temperature. This is in agreement with qualitative results reported in the literature (19, 52).

The yields of pulp at 50, 80, 90 and 95% delignification for each run were read from the curves in Fig. 34, and replotted against the temperature in Fig. 35. The horizontal dotted lines represent the maximum yields possible at the respective lignin contents, calculated as the sum of the lignin plus the original non-lignin content of the wood (72.5%). It is observed that the actual yields approach their maximum values at temperatures below 70°C. That is, very little or no carbo-

TABLE 25

The Effect of Temperature on the Rate of Delignification of Spruce Wood and Yield of Pulp

Wood:- spruce meal, 40-100 mesh. Density 0.43. Extracted in Soxhlet 12 hr., alcohol-benzene (1:2). Lignin 27.5%, extracted wood basis.

Cooking:- Pyrex bombs, calcium base liquor.

I	II	III	IV	V	VI	VII	VIII
Time in bath (uncorr.), hours	Comb. SO_2, %	Total SO_2 (uncorr.), %	Total SO_2 (corr.), %	Yield of pulp, %	Yield of non-lignin, %	Lignin, % of pulp	Lignin, % of orig. wood
Run No. 70. Temperature 50°C.							
150	0.95	10.40	10.40	91.6	74.4	18.8	17.2
310	0.95	10.20	10.20	87.8	75.7	13.8	12.1
500	0.95	10.50	10.50	85.6	77.1	9.91	8.48
910	0.98	10.50	10.50	78.7	76.3	2.98	2.35
1510	0.92	10.30	10.30	73.5	72.6	1.23	0.90
Average	0.96	10.38	10.38				
Run No. 93. Temperature 70°C.							
36	0.97	11.08	11.08	87.1	71.1	18.4	16.0
72	0.94	10.96	10.96	81.6	71.7	12.2	9.91
96	0.94	10.96	10.96	78.8	72.3	8.14	6.46
120	0.92	10.78	10.78	75.3	70.5	6.31	4.75
144	0.92	10.72	10.72	72.3	69.6	3.76	2.72
180	0.90	10.58	10.58	69.3	67.8	2.10	1.45
216	0.94	10.82	10.82	66.8	65.9	1.34	0.90
Average	0.93	10.84	10.84				

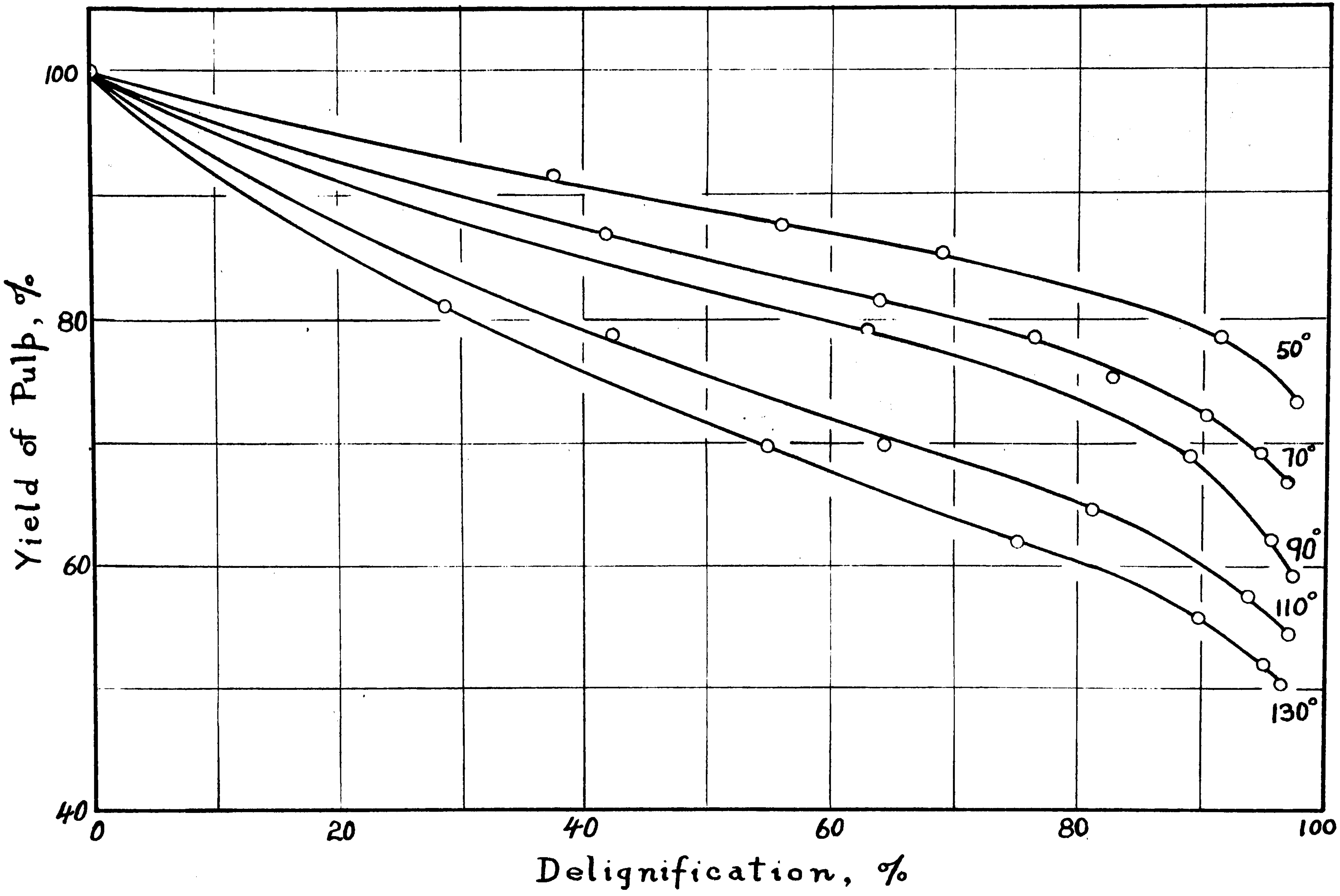


Fig. 34. The effect of temperature on the yield of pulp. Calcium base sulphite liquor; average combined 0.92%, average free sulphur dioxide 9.75%.

TABLE 25 (continued)

I	II	III	IV	V	VI	VII	VIII
Run No. 79. Temperature 90°C.							
12.0	0.98	10.88	10.87	79.3	69.1	12.9	10.2
24.0	0.95	10.84	10.82	69.0	66.0	4.39	3.03
36.0	0.94	10.88	10.85	62.2	61.0	1.97	1.23
48.2	0.95	10.68	10.66	59.3	58.5	1.26	0.75
Average	0.95	10.82	10.80				
Run No. 89. Temperature 110°C.							
2.00	0.94	10.60	10.55	78.7	62.8	20.2	15.9
4.00	0.94	10.60	10.53	69.7	59.9	14.0	9.77
5.50	0.90	10.72	10.62	64.6	59.5	7.97	5.14
8.00	0.90	10.88	10.80	57.5	55.8	2.97	1.71
10.00	0.90	10.92	10.82	54.4	53.6	1.47	0.80
Average	0.91	10.74	10.66				
Run No. 55. Temperature 130°C. See Table No. 20, page 111.							

hydrate material is removed from the wood at these low temperatures, even though delignification is complete. This shows another fallacy in Stangeland's argument (see page 21), that there must be a union between lignin and carbohydrates, because both appeared to go into solution at the same rate. This is not the case at low cooking temperatures, since lignin can be removed from the wood leaving the carbohydrates intact.

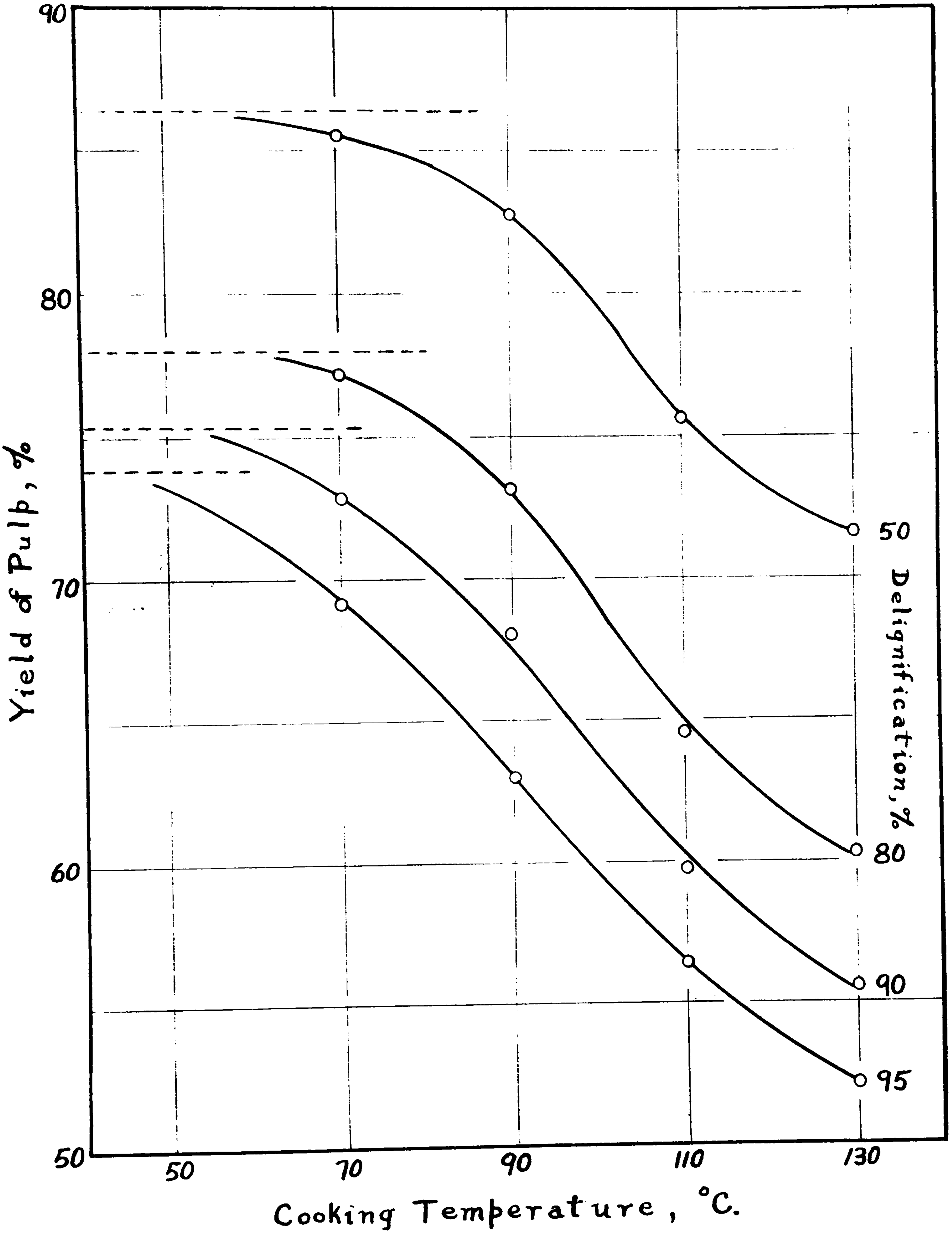


Fig. 35. The effect of temperature on the yield of pulp. Calcium base sulphite liquor; average combined 0.92%, average free sulphur dioxide 9.75%.

It should be mentioned that the yields of non-lignin reported at 50°C. in Table 25 appear to be anomalous, as they are slightly higher than the non-lignin content of the original wood (72.5%). The only explanation would seem to be that the lignin values are in error, because the non-lignin is obtained by difference. However, the lignin analysis was done in duplicate for this particular run and good checks were obtained. The difference is consistent, not accidental, and due possibly to some peculiar effect of low temperature cooking on the residual lignin. This anomaly is being investigated further by Cannon (12).

The yield vs. temperature curves in Fig. 35 show a slight tendency to flatten out at the higher temperatures. This is to be expected, since some of the carbohydrate material (alpha-cellulose) is much more resistant than the remainder. Only extremely severe or prolonged cooking would reduce the yield of pulp below 40%. Nevertheless, it is clear that temperatures of 150°C., which are sometimes reached in commercial pulping, would be extremely harmful from the point of view of yield.

Yorston (75) has shown that under certain cooking conditions, the loss of non-lignin may be expressed by the following empirical equation:

$$\text{loss of non-lignin} = k\,t^{n} \quad \ldots\ldots\ldots\ldots\ldots \quad (19)$$

where t = the time of cooking,
k = a constant, and
n = a constant.

The results reported in Table 25 did not fit this equation well, and the exponent varied with the temperature. Consequently, it was impossible to calculate the temperature coefficient for the removal of non-lignin, nor to extrapolate accurately to higher temperatures. In any case, this would be difficult because non-lignin is a heterogeneous material and varies in its resistance to attack. In addition, the hydrogen ion concentration of sulphite liquor, which plays an important role in carbohydrate degredation, changes in a marked manner with the temperature, even though the liquor composition remains unaltered (4, 32).

The practical advantage of very low cooking temperatures in increased yields of pulp is offset by the long time required for cooking. Also, much of the less resistant carbohydrate material, which is not removed at the lower temperatures, is of little use to the paper maker. However, an intermediate cooking temperature of, say, 90°C. using a liquor high in free sulphur dioxide, might result in a considerable improvement in quality, as well as a high yield of pulp.

2. The Temperature Coefficient of Delignification

The lignin remaining in the pulp at each temperature, as percent of the original wood, is plotted on a logarithmic scale against the observed time of cooking in Fig. 36. The same deviation from the first order relation mentioned previously is

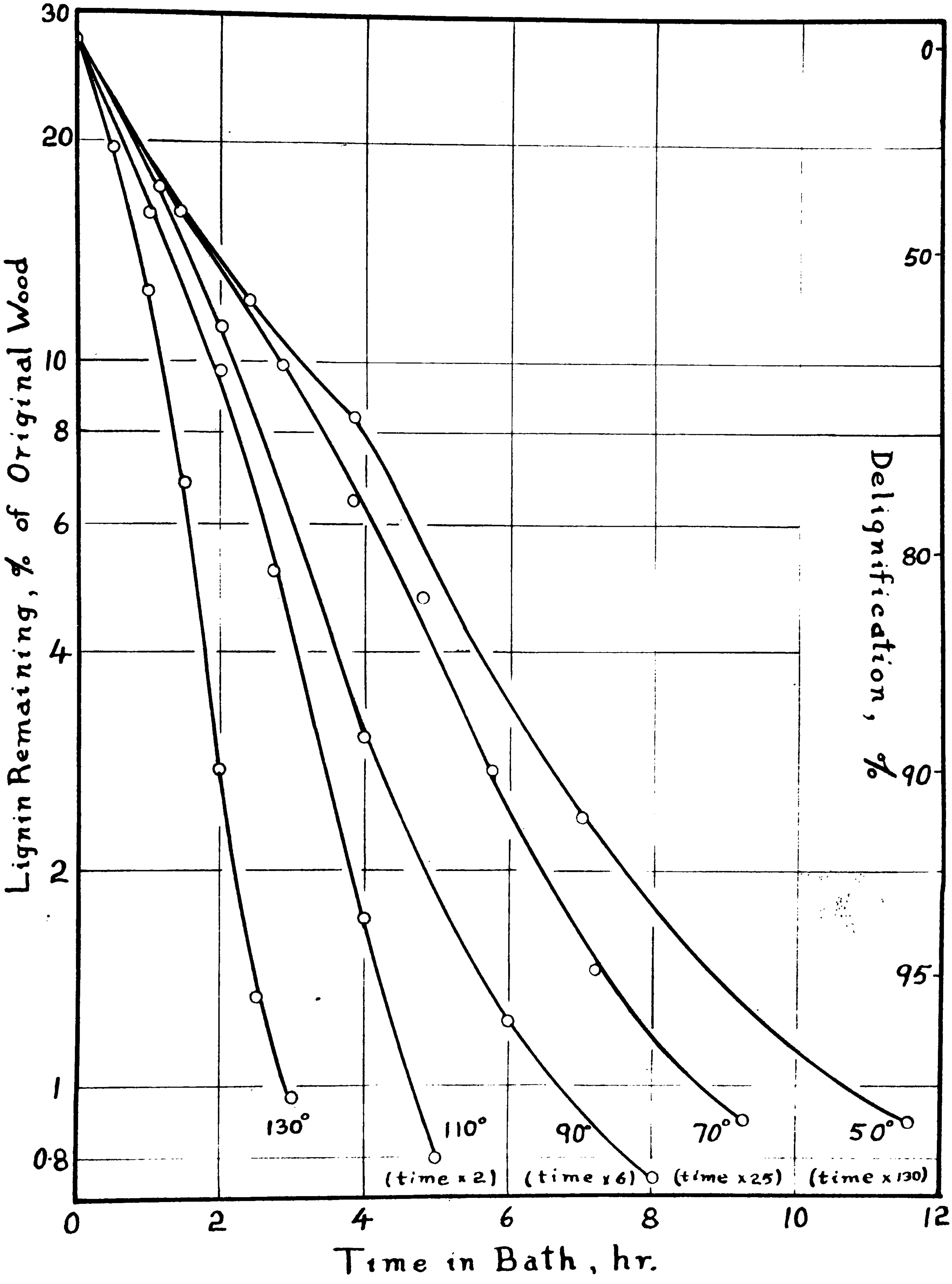


Fig. 36. The effect of temperature on the rate of delignification of spruce wood. Calcium base sulphite liquor; average combined 0.92%, average free sulphur dioxide 9.75%.

apparent here. The delignification curves are all similar in shape with the exception of the one obtained at 50°C. In this case, the first portion of the curve appears to fall too rapidly, i.e., the lignin values seem somewhat too low. This is in agreement with the anomaly already mentioned regarding the impossibly high values of non-lignin reported for this run. In the latter stages of the reaction the lignin values appear to be more consistent.

This run at 50°C. might well have been omitted, but for the interest in such a low temperature cook. It proves conclusively that wood can be completely delignified by the sulphite process at temperatures this low, a fact which is contrary to general belief. Although the 50°C. cook has been included in the calculations of the temperature coefficient, a reservation must be made regarding the validity of the velocity constants for this particular run until further investigation has been made.

The calculation of the temperature coefficient of delignification is rendered difficult by the deviation of the reaction from the first order relation, since an estimation of velocity constants is necessary. However, the following method was adopted:

The observed time required to bring about 50, 80, 90 and 95% delignification at each temperature was read from the curves in Fig. 36, and is given in Table 26. The time correction was then applied for the cooks at 110 and 130°C. by

TABLE 26

Calculation of Velocity Constants and the Temperature Coefficient of Delignification

Temperature, °C.	50	70	90	110	130
Average concentration of sulphur dioxide (corrected), %.					
Combined	0.96	0.93	0.95	0.91	0.87
Total	10.38	10.85	10.80	10.66	10.65
Free	9.42	9.92	9.85	9.75	9.78
Time, (observed), hr.					
To 50% delignification	245	48	8.80	2.59	0.90
To 80% "	655	109	18.4	5.36	1.64
To 90% "	855	143	25.1	6.80	2.00
To 95% "	1180	184	33.8	8.45	2.47
Time (corrected for time required to reach temperature), hr.					
To 50% delignification	245	48	8.80	2.41	0.68
To 80% "	655	109	18.4	5.18	1.42
To 90% "	855	143	25.1	6.62	1.78
To 95% "	1180	184	33.8	8.27	2.25
Time (corrected to 9.75% free sulphur dioxide), hr.					
To 50% delignification	237	48.8	8.88	2.41	0.68
To 80% "	632	111	18.6	5.18	1.42
To 90% "	826	145	25.3	6.62	1.78
To 95% "	1140	187	34.1	8.27	2.25
First order velocity constants, $k \times 10^5$ (seconds^{-1}).					
0-50% delignification	0.0813	0.395	2.17	7.99	28.3
50-80% "	0.0644	0.410	2.62	9.19	34.4
80-90% "	0.0997	0.567	2.87	13.37	53.5
90-95% "	0.0613	0.459	2.19	11.67	41.0
Average	0.0767	0.458	2.46	10.56	39.3

Temperature coefficient per 10°C. 2.44 2.32 2.07 1.93

subtracting 0.18 and 0.22 hours respectively from the observed times. Finally, all the times were corrected to correspond to cooking with the same concentration of free sulphur dioxide (9.75%). This was necessary because it was impossible to predetermine the exact liquor composition, and small variations resulted. This correction was readily made, since it has been shown that the time of cooking at constant combined, is inversely proportional to the free sulphur dioxide, at least over short ranges.

The corrected times, so obtained, are all reported in Table 26. First order velocity constants were then calculated at each temperature according to Equation (2), page 20, for the ranges 0 to 50%, 50 to 80%, 80 to 90%, and 90 to 95% delignification, all expressed in units of seconds $^{-1}$ These velocity constants are listed in Table 26, and differ considerably at different stages in the cooking process at any one temperature, as expected. The variation is systematic, not haphazard, and is due to the regular deviation of the reaction from the first order relationship. However, it is believed that the mean velocity constants, calculated in the same manner at each temperature, represent as fair a value as it is possible to obtain.

The approximate temperature coefficient per ten degrees was calculated for each interval according to the empirical equation:

$$\begin{array}{c}\text{Temperature}\\\text{coefficient}\\\text{per 10°C.}\end{array} = \left[\frac{k_2}{k_1}\right]^{10/(t_2-t_1)} \quad \ldots\ldots\ldots\ldots (20)$$

where $k_2 =$ the velocity constant at the higher temperature, t_2°C.
$k_1 =$ the velocity constant at the lower temperature, t_1°C.

The calculated values are shown at the bottom of Table 26. It is observed that they are close to 2, but decrease with increasing temperature. This is due to the fact that Equation (20) is only a rough approximation of the true temperature coefficient. However, it does show that the reaction velocity approximately doubles for every 10°C. increase in temperature, which is in agreement with previous reports (18, 66).

A more accurate measure of the temperature coefficient of a chemical reaction is given by the Arrhenius equation:

$$\frac{d \ln k}{d T} = \frac{E}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

where $k =$ the velocity constant,
$T =$ the absolute temperature,
$R =$ the molar gas constant in cal. per degree,
$E =$ a constant.

On integration, Equation (21) becomes:

$$\ln k = \ln Z - E/RT \quad \ldots\ldots\ldots\ldots \quad (22)$$

or

$$k = Z\, e^{-E/RT} \quad \ldots\ldots\ldots\ldots \quad (23)$$

where $Z =$ a constant.

If the Arrhenius equation holds for a given reaction, it is obvious that a plot of the logarithm of the velocity constant against the reciprocal of the absolute temperature will give a straight line. Fig. 37 shows the mean velocity constants for

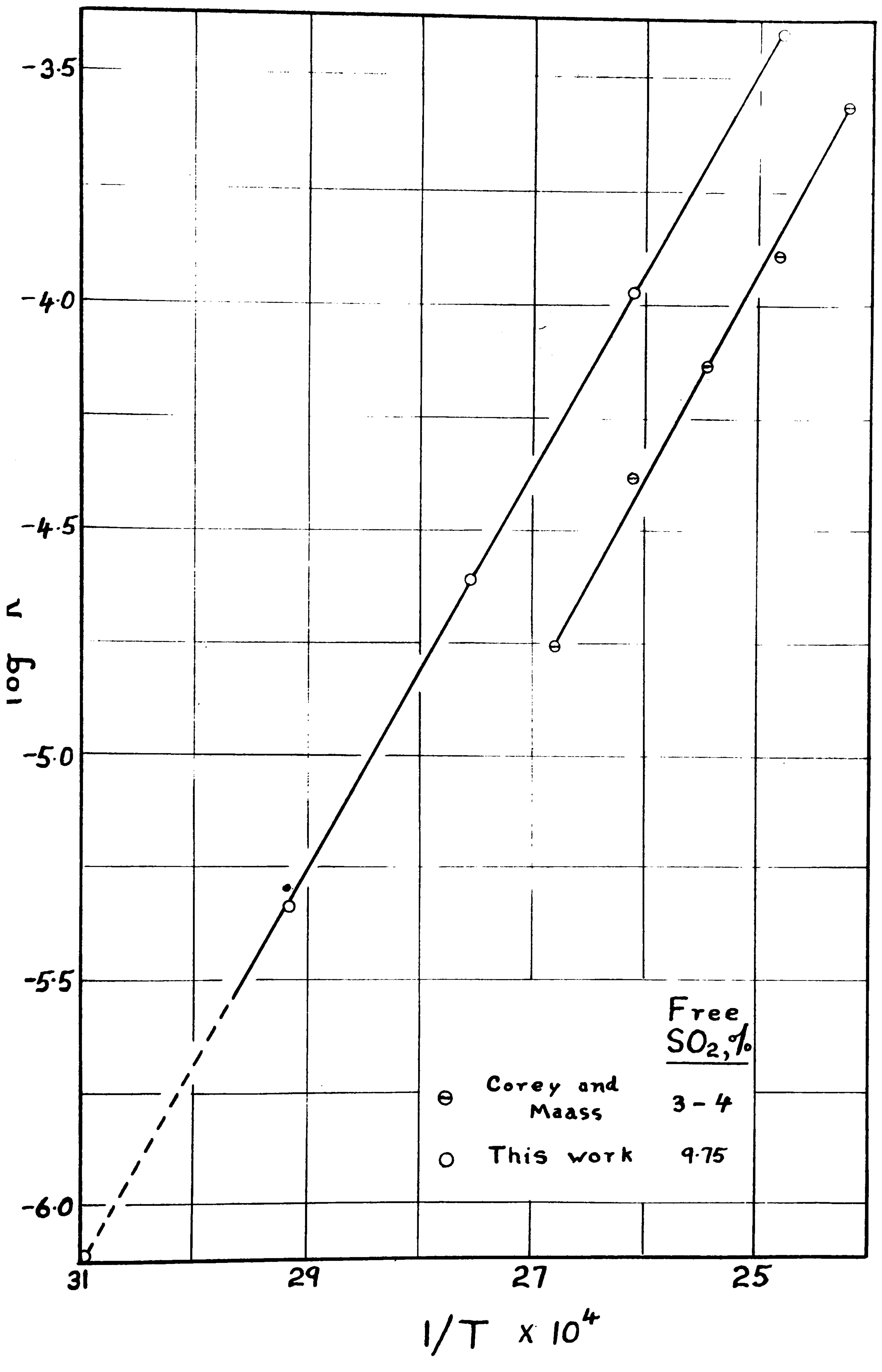


Fig. 37. The temperature coefficient of the delignification of spruce wood in calcium base sulphite liquor.

the delignification of wood, calculated as described above, plotted according to this relation. It is observed that an excellent straight line is obtained over the whole temperature range.

The temperature coefficient curve for the delignification of spruce wood-meal in sulphite liquor reported earlier by Corey and Maass (18) is also plotted in Fig. 37. Their data were converted from hours^{-1} to seconds^{-1} for comparison. The magnitude of the velocities in the two cases differs because different liquor concentrations were used. The important point is that the slopes of the temperature coefficient curves (and hence, the values of "E") are very nearly the same in both cases. It is believed that greater accuracy has been achieved in the present work, since the improved experimental technique permitted closer control of the liquor concentration and the temperature. In addition, Corey made only two individual cooks for each run, and investigated a much shorter range of temperature.

The constants of the Arrhenius equation for the reaction reported here were calculated from the straight line in Fig. 37, and found to be:

$$E = 20,170 \text{ cal. per gm. mol.}$$

$$Z = 3.42 \times 10^{7} \text{ sec.}^{-1}.$$

The value of "E" reported by Corey and Maass is 21,000 cal. per gm. mol., which is good agreement considering the errors involved. The constant "Z", of course, depends on the concentration of the cooking liquor.

By substituting the values of "E" and "Z" obtained here into Equations (22) and (23), corresponding equations are obtained which express the variation in the reaction velocity with temperature for the sulphite process under the experimental conditions chosen:

$$\ln k = 17.3 - 20{,}170/RT \quad \text{..........} \quad (22,\ a)$$

or

$$k = 3.42 \times 10^{7}\ e^{-20{,}170/RT} \quad \text{.........} \quad (23,\ a)$$

The observed values of "k" are compared in Table 27 with values calculated from Equation (23,a). It is observed that good agreement is obtained. The possible theoretical significance of the constants "E" and "Z" for this reaction will be discussed in a later section.

TABLE 27

The Delignification of Spruce Wood in Calcium Base Sulphite Liquor

t°C.	$k \times 10^5$ (seconds^{-1})	
	Observed	By the Arrhenius Equation
50	0.0767	0.0767
70	0.458	0.479
90	2.46	2.45
110	10.56	10.55
130	39.3	39.3

The fact that the delignification of wood in sulphite liquor obeys the Arrhenius equation rigidly over the whole temperature range investigated, shows that the mechanism of the reaction must be the same at low, as well as high temperatures. There is no critical temperature such as 110°C. (as frequently claimed), below which the delignification reaction does not proceed normally. The temperature appears to affect only the velocity of delignification, as in the case of comparatively simple homogeneous reactions. This statement holds, even if we consider the velocity constant calculated at 50°C. unreliable for the reasons previously mentioned. The cooks made at 70°C., and 90°C. provide sufficient evidence that the reaction obeys the Arrhenius equation below 110°C.

SUMMARY OF RESULTS (PART II)

The Rate of Delignification of Spruce Wood

(Resin extracted wood-meal cooked at high liquor ratio under conditions of constant volume, constant temperature, and constant concentration).

1. The rate of delignification of spruce wood in calcium base sulphite liquor at 130°C. is practically independent of the concentration of combined sulphur dioxide between 0.25 and 1.0%, when the free sulphur dioxide is constant.

2. The rate of delignification of spruce wood in calcium base sulphite liquor at 130°C. is proportional to the concentration of free sulphur dioxide between 1.5 and 13%, but increases less rapidly at the higher concentrations. The curve extrapolates to zero rate of reaction at zero concentration of free sulphur dioxide.

3. The partial pressure of sulphur dioxide gas over calcium base sulphite liquor at 130°C. gives a better relation with the rate of delignification than the analytically determined concentration of free sulphur dioxide. The logarithm of the partial pressure of sulphur dioxide vs. the logarithm of the rate of delignification gives one straight line for three series of combined sulphur dioxide.

4. The pH of calcium base sulphite liquor at 130°C. vs. the logarithm of the rate of delignification gives three distinctly separate, almost parallel straight lines for the three series of combined sulphur dioxide.

5. The rate of delignification of spruce wood in magnesium base sulphite liquor at 130°C. is not independent of the concentration of combined sulphur dioxide, when the free sulphur dioxide is constant, but decreases with increase in the combined between 0.5 and 4.0%. The decrease in the rate of reaction is very rapid above 2% combined when the free sulphur dioxide is constant.

6. The rate of delignification of spruce wood in magnesium base sulphite liquor at 130°C. is proportional to the concentration of free sulphur dioxide between 2 and 10%, when the combined sulphur dioxide is constant, but increases less rapidly at the higher concentrations. The concentration of free sulphur dioxide extrapolated to zero rate of delignification is greater than zero, and increases with increase in the concentration of combined sulphur dioxide.

7. The rate of delignification of spruce wood at 130°C. in solutions of magnesium bisulphite containing no excess sulphurous acid is small, but increases slowly with increasing concentration of magnesium bisulphite.

8. The rate of delignification of spruce wood in magnesium

base sulphite liquor at 130°C. cannot be expressed by any simple relation of the type:

$$\text{rate} = K\,(\text{total } SO_2 - n \text{ comb. } SO_2)$$

where "K" and "n" are constants.

9. The rate of delignification of spruce wood at 130°C. is definitely greater in magnesium base sulphite liquor, than in calcium base sulphite liquor of the same mole percent composition.

10. The shape of the delignification curve when plotted according to the first order relation is the same for all concentrations of combined and free sulphur dioxide investigated, for both calcium and magnesium base sulphite liquor.

11. The relation "$L^{1/3}$ vs. time" gives better agreement with the experimental data for the delignification of spruce wood in both calcium and magnesium base sulphite liquor for 95% of the reaction, than does the first order relation. In the final stages of cooking the velocity of delignification is less than predicted by either relation.

12. The variation in the rate of delignification of spruce wood with temperature obeys the Arrhenius equation from 130°C. down to 70°C. or lower, the rate being approximately halved for every 10°C. decrease in temperature. The value of the constant "E" for the reaction is 20,170 cal. per gm. mol.

13. Spruce wood can be completely delignified by the sulphite process at temperatures as low as 50°C.

The Yield of Pulp

14. When spruce wood is cooked in either calcium or magnesium base sulphite liquor, the yield of pulp at a given lignin content is virtually independent of the concentration of free sulphur dioxide, but increases rapidly at first and then more slowly with increase in the concentration of combined sulphur dioxide. In the case of magnesium base cooks, the yield reaches a maximum value at about 3% combined sulphur dioxide and decreases somewhat at higher concentrations.

15. The yield of pulp is somewhat greater from magnesium base cooks than from calcium base cooks made under the same conditions (except at low concentrations of combined sulphur dioxide).

16. Yields of pulp higher than 55% of the original wood have been obtained with 90% removal of lignin at 130°C. and 1% combined sulphur dioxide. This is considerably greater than is found in commercial sulphite pulping.

17. The yield of pulp at a given lignin content decreases rapidly with increase in the cooking temperature. At 70°C. and lower, the lignin can be completely removed from the wood leaving nearly all of the carbohydrate intact.

GENERAL DISCUSSION AND CONCLUSION (PART II)

An attempt will now be made to correlate the experimental findings in regard to the effect of liquor composition and temperature on the velocity of delignification. It was pointed out in the introductory section that any elucidation of the mechanism of this reaction at the present time is rendered difficult by the uncertainty regarding the nature and structure of lignin. Nevertheless, it is believed that a theoretical discussion is of value in providing an impetus for further research, even should the interpretation of the experimental facts require revision as our knowledge of the chemistry of lignin increases.

The Effect of Liquor Composition on the Rate of Delignification

It has been shown in the present work that the rate of delignification of spruce wood-meal in calcium base sulphite liquor is proportional to the partial pressure of sulphur dioxide gas and is independent of the concentration of base, at least over the range permitted by its solubility. Evidence that the active cooking agent appears to be free sulphurous acid or the hydrogen and bisulphite ions together (not either ion alone) has been given. From the results of the magnesium base cooks there is some reason to believe that this relationship may not hold at high concentrations of combined sulphur dioxide, but until the vapor pressures and ion concentrations of the magnesium system are known we cannot be certain.

The delignification mechanism proposed by Hägglund is based on the assumption of a rapid sulphonation reaction, followed by the hydrolysis of a hypothetical lignin-sulphonic-carbohydrate compound, the rate of which is governed by the hydrogen ion concentration of the liquor and determines the overall rate of delignification. This theory is quite untenable in the light of the evidence presented here. We have shown that the rate of delignification is not controlled by the hydrogen ion concentration alone, even in the final stages of the reaction when the lignin is highly sulphonated. Hägglund's emphasis of the hydrogen ion concentration as determining the rate of delignification, is based chiefly on the indirect evidence that sulphonated lignin remaining in partially cooked wood can be removed by heating in buffer solutions in the absence of sulphites at a rate depending on the pH of the buffer. Although this is quite true for cooking continued in buffer solutions, we have shown that it does not hold for continued delignification in sulphite liquor.

In addition, there is little, if any, experimental evidence of a bond between lignin and carbohydrate material. Either one can be removed from the wood by various methods leaving the other intact, although the supporters of Hägglund maintain that all such methods of isolation rupture the bond. This, however, does not prove its existence. In any case, even if there is a bond between lignin and carbohydrates which is broken by hydrolysis during cooking, we have shown that this does not satisfactorily account for the removal of lignin.

Kullgren (46) has proposed a slightly different mechanism for the delignification of wood in sulphite liquor which is equally untenable. He suggests that there is an equilibrium between the free sulphonic acid and its calcium salt and that only the former is soluble. Kullgren also maintains that the rate of delignification is determined by the ratio of the hydrogen ion concentration to the calcium ion concentration, i.e., $(H^+)/(Ca^{++})$. The results obtained in the present work show that this is not true. When the concentration of base is kept constant, the rate of reaction does increase with increase in the hydrogen ion concentration. However, an increase in the concentration of base also increases the rate of delignification, provided the hydrogen ion concentration is held constant. This is exactly the reverse of what Kullgren's theory would predict, and is due to the fact that he has ignored the important role played by the bisulphite ion.

Whether we accept the hypothesis of two consecutive reactions or not, it seems clear that the rate of delignification depends on the concentration of dissociated or undissociated sulphurous acid, provided a certain minimum concentration of base is present. It is possible that the sulphonation reaction is the rate determining reaction, although this is contrary to the beliefs of Hägglund. The question then arises, why does the reaction rate decrease in the latter stages of cooking when the sulphur content of the residual lignin is high? This would be explained if all of the sulphur were not combined with the lignin in a form which assists delignification. Klason (43) maintains that this is true, only part of the sulphur being present as sulphonic acid groups and the remainder being loosely combined.

Let us suppose, then, that delignification does consist essentially of a reaction between lignin and sulphurous acid. We shall ignore the heterogeneous nature of the reaction for the moment and treat it as a simple homogeneous reaction involving two molecular species. This is not as unjustifiable as it may seem, because of the strong evidence (see page 82) that all parts of the lignin are accessible to the reagent. Lignin has a number of gel-like properties, and it is quite possible that small solute molecules can diffuse through any part of it almost as readily as through the solution. This only applies, of course, to the cooking of finely divided wood-meal where penetration factors are not involved. The lignin may be conveniently pictured as existing in a number of repeating units or aggregates of unknown size, which in the presence of a peptizing medium may undergo slight molecular motion within the confines allowed by the structure as a whole.

The rate of formation of lignin sulphonic acid should therefore be given by the following equation:

$$\frac{dx}{dt} = k_2 (a-x)(b-x) \qquad \ldots\ldots \quad \ldots\ldots\ldots \quad (24)$$

where a = the initial "concentration" of lignin,
b = the initial concentration of sulphurous acid,
x = the amount transformed in time "t",
k_2 = the velocity constant.

This is the ordinary equation for a bimolecular reaction.

However, the concentration of sulphurous acid under the conditions of our experiments is so much greater than the "concentration" of lignin in the system, that we can consider the term (b-x) as approximately constant and equal to "b". Equation (24) then becomes:

$$\begin{aligned} \frac{dx}{dt} &= k_2 (a-x)b \\ &= k_{obs} (a-x) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (25) \end{aligned}$$

where k_{obs} = the observed velocity constant.

In other words, the reaction is merely pseudo-unimolecular, and Equation (25) is essentially the same as Equation (1, p.20), derived on the basis of a first order reaction. The relation between the true bimolecular constant and the observed velocity constant would then be given by the equation:

$$k_2 = \frac{k_{obs}}{b} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (26)$$

This would indicate a linear relation between the rate of delignification and the concentration of free sulphur dioxide, which is not quite borne out by experiment. Actually the exponent in Equation (17, p.124) is 0.84 (i.e., not far from unity), and we can consider the relation as approximately linear for the purposes of the present discussion.

One criticism of the hypothesis of a pseudo-unimolecular reaction might be made on the grounds that no difference in the shape of the delignification curve was observed between cooks made at low and high concentrations of free sulphur dioxide.

However, even when cooks are made with the customary liquor ratio of 5:1 (one tenth of that used in the present work), there is still a large excess of sulphurous acid. We would not expect any bimolecular tendency to show up under these conditions.

The Temperature Coefficient of Delignification

Consider, now, the evidence of the temperature coefficient of delignification. The fact that the reaction obeys the Arrhenius equation rigidly over a considerable temperature range, and inspite of all of the complex factors involved, is very significant. The Arrhenius equation is based on the activation theory of molecular collisions. According to this theory, which forms the foundation of chemical dynamics, a molecule undergoes chemical transformation only when it is in an activated state brought about by the acquisition of energy by collision in excess of a certain minimum. This minimum, or critical energy is called the energy of activation and designated "E".

In the case of bimolecular reactions, the rate of reaction will be equal to the number of collisions multiplied by the fraction of these which are effective, i.e., it will be equal to the number of activating collisions. In the Arrhenius equation

$$k = Z\ e^{-E/RT},$$

the constants immediately take on a new significance. "Z" is the number of collisions occurring per cc. per second between the two types of molecules, and $e^{-E/RT}$, according to the Maxwell-Boltzmann distribution law, is the fraction of these possessing critical energies of "E" or more. This theory has received ample verification from a study of the kinetics of homogeneous reactions in the gaseous phase, and Moelwyn-Hughes (54) has shown that it is fundamentally true for reactions in solution.

The theoretical value of the collision frequency between molecules of types 1 and 2 (the constant "Z" of the Arrhenius equation) may be calculated from an expression given by Moelwyn-Hughes derived from the kinetic theory:

$$Z = \frac{N_0}{1000} s_{1,2}^2 \left[8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{1/2} \quad \text{..... .....} \quad (27)$$

where N_0 = Avogadro's number,
s = the molecular diameter and $s_{1,2} = 1/2(s_1 + s_2)$,
R = the molar gas constant in ergs per degree,
T = the absolute temperature,
M = the molecular weight.

The theoretical value of "Z" for <u>all</u> uncomplicated bimolecular reactions in solution is of the order of 10^{11} seconds^{-1}. This is due to the compensating effect of two opposing factors, which can be seen in Equation (27). Large molecules move more slowly, but have a relatively large cross-sectional area; small molecules have a higher velocity, but a smaller collision area. Consequently, the theoretical collision frequency is approximately constant, and the theoretical reaction velocity will be determined by the energy required for activation.

By combining Equation (27) with the Arrhenius equation, an important expression is obtained which is referred to as the equation of Lewis:

$$k_2 = \frac{N_o}{1000} s_{1,2}^2 \left[8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{1/2} e^{-E/RT} \quad .... (28)$$

This gives the theoretical reaction velocity of an uncomplicated bimolecular reaction, where "k_2" is expressed in liters per gram molecule per second. Moelwyn-Hughes has compared 181 bimolecular reactions in solution, the energies of activation of which have been determined with sufficient accuracy. He found that more than 40% of these have normal velocities, i.e., they have velocities very nearly equal to those predicted by Equation (28). Of the remainder, some have higher velocities and some lower. In these cases, there are a number of plausible reasons for the discrepancy from the theoretical value. Hence, by comparing the experimental value of "Z" for a given reaction with the theoretical value, an important clue to the mechanism may be obtained.

In the case of the delignification of spruce wood-meal in calcium base sulphite liquor (containing 9.75% free sulphur dioxide), the bimolecular velocity constants may be calculated from the observed velocity constants by means of Equation (26). The value of "b" is 1.52 moles per liter. The experimental value of "Z" under conditions comparable with Equation (27) will then be:

$$Z = \frac{3.42 \times 10^7}{1.52} = 2.25 \times 10^7 \text{ seconds}^{-1}.$$

In other words, the collision frequency appears to be lower than the theoretical value by a factor of 10^4. Or rather, only one collision in 10,000 having the requisite energy (20,170 cal.

per gm. mol.) results in reaction.

This abnormally low velocity has been observed with a number of relatively simple reactions in solution known to be bimolecular. Moelwyn-Hughes offers a number of explanations for this, the most probable of which in the present case is that stringent conditions of orientation are required. This is a reasonable explanation in view of the size and complexity of the lignin molecule. Only when an activating collision occurs at a certain point in the molecule will reaction take place and a sulphonic acid group be introduced.

The value of the critical energy "E" found for the sulphite process (20,170 cal. per gm. mol.) is of the same order of magnitude as that for homogeneous bimolecular reactions in solution It may not be the true energy of activation for the reaction between lignin and sulphurous acid. If there is an endothermic or exothermic formation of an intermediate complex, or if an adsorption process occurs, the observed value of "E" will be the algebraic sum of the heat of formation of the complex or the heat of adsorption and the true energy of activation of the reaction. In the case of the delignification of wood by the alkali process, Larocque (47) has calculated a critical energy of 32,000 cal. per gm. mol. The higher value of "E" explains the higher temperature required for the successful pulping of wood by the alkali process.

The Rate of Delignification at a Fixed Liquor Composition

Since there is always a large excess of sulphurous acid present during the delignification reaction, we would expect the instantaneous rate of removal of lignin in any one sulphite liquor to be proportional to the quantity of lignin remaining undissolved (i.e., a first order reaction), provided:

(a) That all of the lignin is equally accessible to the reagent.

(b) That the lignin is chemically homogeneous.

(c) That only one chemical reaction takes place; or if there are a series of-consecutive reactions, one reaction is slow enough in comparison with the others to be rate determining.

Experimentally, the delignification reaction closely approximates, but does not exactly follow the monomolecular law. The regular deviations from the first order relationship cannot be due to the consumption of sulphur dioxide as the reaction proceeds, since the shape of the delignification curve was found to be the same for all of the liquor concentrations tried over a wide range. In addition, the analysis of the liquor after cooking showed that only very slight concentration changes occurred during cooking. The deviation is therefore real and not due to errors in technique.

The evidence is fairly strong that all of the lignin is accessible to the reagent. Hence, the consistant deviation of the reaction from the first order relationship may be due to the non-fulfilment of conditions (b) or (c). Since lignin is a complex biological product there is reason to believe that it is not chemically homogeneous. Lignin sulphonic acids recovered from waste liquor can be separated into two distinct fractions, although it has been suggested that the difference is one of molecular aggregation rather than chemical behaviour. In addition, the decrease in rate toward the end of the reaction has frequently been attributed to the existence of a more resistant fraction of lignin.

As mentioned in the historical section, Yorston has developed the hypothesis of two consecutive monomolecular reactions, and has shown that the shape of the delignification curve can be explained on this basis, provided that the velocity constants of the two reactions do not differ by more than a factor of about two. It was suggested that the rate of sulphonation might be proportional to the quantity of unsulphonated lignin present at any instant, and that the rate of removal of lignin might be proportional to the quantity of sulphonated lignin present at any instant. However, it was found that the actual rate of removal of lignin could not be predicted in this manner, and it was concluded that more sulphur was taken up by the lignin than is required for delignification.

Evidence of Heterogeneity

Although in many ways the lignin appears to be completely accessible to the cooking reagent, there is evidence from the experimental results reported here that lignin in finely divided wood-meal is somewhat less accessible to the reagents than a reactant in true solution. In other words, surface effects may be involved and it may be necessary to consider delignification from the point of view of a heterogeneous reaction. The evidence in support of this may be summarized as follows:

(i) It has been shown that the rate of delignification of wood-meal in sulphite liquor may be represented more accurately by the relation "$L^{1/3}$ vs. time", than by the first order relation. The former relation was derived on the hypothesis that lignin might exist in wood in approximately spherical particles, and that the rate of cooking was determined by the variation in the exposed surface area of the particles. Since other explanations for the deviation of the reaction from the monomolecular law are equally plausible, this cannot be considered strong evidence.

(ii) A second fact which suggests that the interface between the lignin and the solution may influence the reaction, is that the relation between the rate of cooking and the partial pressure of sulphur dioxide (for calcium base liquor) follows the Freundlich adsorption isotherm. If the concentration of sulphurous acid at the lignin surface were greater than in the body of the solution, this relationship would be accounted for. However, it was mentioned that the exponent (0.84) in Equation (17) does not depart greatly from unity, and other possible explanations have been offered (page 123) to account for the shape of the rate vs. partial pressure curve.

(iii) The Arrhenius equation for the delignification of wood-meal in sulphite liquor shows that the velocity of the reaction is abnormally low, and suggests that orientation or stearic hindrance is involved. Molecules in true solution sometimes exhibit this abnormal behaviour, but it might also be attributed to heterogeneity. On the other hand, the temperature coefficient of delignification is definitely that of a chemical reaction, not of a diffusion process. The velocity is therefore not determined by the latter, and diffusion of the reactants and products must be more rapid than chemical reaction.

It must be admitted that the evidence of heterogeneity in the delignification of finely divided wood-meal is weak, although of course penetration and diffusion factors are involved in the case of chips. Because of the colloidal nature of lignin, it is only natural that the cooking process should exhibit characteristics of both homogeneous and heterogeneous reactions, and there is evidence to justify both points of view.

Conclusion

There are still a great many facts about the delignification of wood by the sulphite process which have not been explained. If delignification consists essentially of a reaction between lignin and sulphurous acid, in what manner does the introduction of sulphonic acid groups render the lignin soluble in the cooking liquor? Why is sulphonated lignin insoluble in water? Since solubility depends on molecular size as well as chemical affinity, there are two ways in which the lignin may be rendered soluble.

Yorston (78) has suggested that the introduction of sulphonic acid groups may confer hydrophile properties on lignin, allowing it to be more easily peptized in a medium of suitable ionic concentration. A depolymerization or rupture of bonds between lignin units may also occur. Both of these processes would tend to increase the solubility of lignin. The greater the depolymerization or the greater the degree of sulphonation, the more readily would the lignin be peptized. Neither process alone seems to be sufficient Incidentally, if a depolymerization of lignin does occur during cooking, as seems reasonable, it is difficult to understand how heating wood in aqueous solutions of similar hydrogen ion concentration would cause a polymerization of lignin, the pros and cons of which have been discussed in the section on pretreatment.

Although, all of the lignin appears to be accessible to sulphurous acid, sulphonation does not take place uniformly, and parts of the lignin become more highly sulphonated than the remainder. Yorston has shown that when the average sulphur content of the lignin is greater than 6%, cooking takes place rapidly in a buffer solution of similar hydrogen ion concentration; when the average sulphur content of the lignin is reduced to 2 to 3%, cooking virtually ceases. Brauns and Hibbert (7A) have presented evidence to show that the minimum molecular weight of a lignin unit may be 872. If this is true, the addition of one sulphonic acid group per lignin unit would give a lignin sulphonic acid containing 3.35% of sulphur. The introduction of a second group would raise the sulphur content to 6.2%. This suggests that only lignin units containing two or more sulphonic acid groups can be removed.

Whether lignin sulphonic acids in waste sulphite liquor contain a fixed quantity of sulphur seems very doubtful. Hawkins, Wright, and Hibbert (35A) have recovered lignin sulphonic acids from waste liquors after cooking a large variety of woods. Their products were purified by dialysis and were found to have an almost constant sulphur content of 5.2 to 5.4%. If this were invariably true, it would be very significant. However, all of the cooks were made under identical experimental conditions, and it is possible that the sulphur content of isolated lignin sulphonic acids depends to some extent on the method of cooking. There is reason to believe that lignin removed during the latter stages of cooking contains a larger amount of sulphur than lignin removed during the early stages. In addition, other investigators (30, 48) have reported lignin sulphonic acids containing 4 to 8% of sulphur. Even the higher figure accounts for only a portion of the sulphur actually consumed during cooking, and it seems probable that side reactions occur in which sulphur is only loosely combined with the lignin and may be split off later during isolation of the sulphonic acids.

Whether there could be any interrelation between the sulphonation reaction and a depolymerization process cannot be stated. However, the observed behaviour of delignification would be difficult to explain on the basis of two independent reactions, each of which assisted in the removal of lignin in a different way. These points cannot be cleared up until we know more about the structure and chemistry of lignin itself.

Although a discussion of the mechanism and kinetics of delignification is highly speculative at the present time, it is nevertheless of value as a means of coordinating experimental data and indicating the most advisable directions for further research. It is hoped that the information provided in this work on the effect of various factors on the rate of delignification of wood-meal in sulphite solutions will be of assistance in the eventual solution of the problem, even if the interpretations attempted here are shown to be incorrect by future investigation. When one considers the complexity of biological substances such as lignin, the great variety of ions and molecules which may be present in the cooking liquor, and the fact that several reactions may be going on simultaneously, it is remarkable that the net delignification process should follow any of the laws which have been found to hold for comparatively simple chemical reactions.

CLAIMS TO ORIGINAL RESEARCH

1. The investigation of the effect of pretreating wood-meal in buffer solutions on subsequent delignification in sulphite liquor has been continued and extended. The effect of pH, temperature, and time of pretreatment has been determined, and the rate of delignification of pretreated wood-meal has been studied.

2. The effect of pretreating wood-meal in a large number of neutral salt solutions has been determined for the first time. The effect on subsequent cooking properties of the concentration of the salt in the pretreating solution and the position of its ions in the lyotropic series has been investigated.

3. A new technique has been devised for determining the rate of delignification of wood-meal in sulphite liquor under conditions of constant volume, constant temperature, and approximately constant liquor concentration. Corrections have been made for the first time for sulphur dioxide which escapes to the vapor phase, and the time required to heat the liquor to the cooking temperature has been accurately determined.

4. The effect of composition of calcium base sulphite liquor on the rate of delignification of spruce wood-meal and on the yield of pulp at 130°C. has been investigated thoroughly for the first time over a wide range of concentration. The combined

sulphur dioxide concentration was varied from 0.25 to 1.5%, and the free sulphur dioxide from 1.5 to 13%.

5. The effect of composition of magnesium base sulphite liquor on the rate of delignification of spruce wood-meal and on the yield of pulp at 130°C. has been investigated for the first time. The combined sulphur dioxide concentration was varied from 0.5 to 4%, and the free sulphur dioxide from 2 to 10%.

6. The rate of delignification of spruce wood-meal in calcium base sulphite liquor has been determined for the first time at temperatures of 50°, 70°, and 90°C.

7. The temperature coefficient of delignification and the energy of activation of the process have been determined more accurately than before, and over a wider temperature range (50° to 130°C.). The effect of temperature on the yield of pulp has also been determined over the same range for the first time.

BIBLIOGRAPHY

(1) Aronovsky, S.I., and Gortner, R.A. J. Ind. and Eng. Chem. 22: 264. 1930.

(2) Aronovsky, S.I., and Gortner, R.A. ibid. 25: 1349. 1933.

(3) Beazley, W. Ph.D. Thesis, McGill University, 1937.

(4) Beazley, W., Campbell, W.B., and Maass, O. Dept. of the Interior, Canada. Forest Service Bull., at press April 1938.

(5) Benson, K.H., Erwin, R.P., Hendrickson, J.R., and Tershin, J.A. T.A.P.P.I. p.513. 1935.

(6) Bergman, J.W. Svensk Pappers-Tid. 38: 215-218. 1935.

(7) Berndt, K. Papier-Fabr. 24: 561, 584. 1926.

(7A) Brauns, F. and Hibbert, H. J. Am. Chem. Soc. 55: 4720-4727. 1933.

(8) Bray, M.W. Paper Trade J. 87 (25): 59. 1928.

(9) Britton, H.T.S. Hydrogen Ions. D. Van Nostrand, New York 1929.

(10) Cable, D.E. Sulphite Pulp from Spruce. T.A.P.P.I. Lockwood Trade J. Co., New York 1928.

(11) Campbell, W.B., and Maass, O. Can. J. Research. 2: 42-64. 1930.

(12) Cannon, J.J.R. Unpublished results, McGill University 1938.

(13) Chidester, C.H. and Billington, P.S. Pulp Paper Mag. Can. 38(3): 241. 1937.

(14) Committee on Vocational Education representing the pulp and paper industry of the United States and Canada. The Manufacture of Pulp and Paper, Vol. III. McGraw-Hill Book Co. Third edition, New York 1937.

(15) Corey, A.J. Ph.D. Thesis, McGill University 1936.

(16) Corey, A.J. and Maass, O. Can. J. Research. B,13: 149-155. 1935.

(17) Corey, A.J. and Maass, O. ibid. B,13: 289-295. 1935.

(18) Corey, A.J. and Maass, O. ibid. B,14: 336-345. 1936.

(19) De Montigny, R., and Maass, O. Dept. of the Interior, Canada. Forest Service Bull. No. 87. 1935.

(20) Freudenberg, K., Belz, W., and Nieman, C. Ber. 62: 1554. 1929.

(21) Freudenberg, K., and Sohns, F. Ber. 66: 262. 1933.

(22) Freudenberg, K., Zocher, H., and Dürr, W. Ber. 62: 1814. 1929.

(23) Gishler, P.E., and Maass, O. Can. J. Research. B,13: 308-322. 1935.

(24) Gishler, P.E., and Maass, O. ibid. B,13: 370-379. 1935.

(25) Gishler, P.E., and Maass, O. ibid. B,14: 301-309. 1936.

(26) Grieve, A.C., and Maass, O. Pulp Paper Mag. Can. 32: 157-160. 1932.

(27) Gurd, G.W., Gishler, P.E., and Maass, O. Can. J. Research. B,13: 209-217. 1935.

(28) Hägglund, E. Papier-Fabr. 24: 775-780. 1926.

(29) Hägglund, E. Papier-Fabr. 27: 165. 1929.

(30) Hägglund, E. Zellstoff. u. Papier. 13: 261-265. 1933.

(31) Hägglund, E., and Carlson, G.E. Biochem. Z. 257: 467. 1933.

(32) Hägglund, E., and Johannson, A. Cellulosechemie. 13: 139-143. 1932.

(33) Hägglund, E., and Johnson, T. Biochem. Z. 202: 439. 1928.

(34) Hägglund, E., and Nihlen, H. Svensk Pappers-Tidn. 37: 754-759. 1934.

(35) Hawkings, C.V.S., and Jentz, Carl Jr. Tech. Sec. Can. Pulp and Paper Assoc. 1930.

(35A) Hawkins, W.L., Wright, G.F., and Hibbert, H. J. Am. Chem. Soc. 57: 2447. 1937.

(36) Hawley, L.F., and Harris, E.E. J. Ind. Eng. Chem. 24: 873-875. 1932.

(37) Hawley, L.F., and Wise, L.E. The Chemistry of Wood. Chemical Catalog. Co. Inc., New York 1926.

(38) Herzog, R.O. and Beck, F. Z. physiol. Chem. 111: 278-292. 1920.

(39) Heuser, E. Textbook of Cellulose Chemistry. Translated from the second German edition by West and Esselen, 1924.

(40) Hiller, O. Papier. 31: 195. 1928.

(41) Hoover, G. I., Hunten, K.W., and Sanky, C.A. J. Phys. Chem. 34: 1361-1386. 1930.

(42) Johnston, H.W., and Maass, O. Can. J. Research. 3: 140-173. 1930.

(43) Klason, P. Ber. 53: 705, 1862, 1864. 1920.

(44) King, T.E. Unpublished results, McGill University 1938.

(45) Kruyt, H.R. Colloids. Wiley and Sons, New York, 1927.

(46) Kullgren, C. Abstract, Paper Industry, p.739. 1934.

(47) Larocque, G. L. Ph.D. Thesis, McGill University 1935.

(48) Lindsey, J.D., and Tollens, B. Ann. 267: 341. 1892.

(49) Maass, C., and Maass, O. J. Am. Chem. Soc. 50: 1352 1928.

(50) McGovern, J. N. Paper Trade J. 103(20): 29-42. 1936.

(51) Michel-Jaffard, R. Papier. 35: 1051. 1932.

(52) Miller, R. N., Swanson, W. H., Bray, M.W., Soderquist, R., Andrews, T. M., and Monsson, W. H. T.A.P.P.I. Lockwood Trade J. Co., New York 1928.

(53) Mitchell, C.R., and Yorston, F. H. Tech. Sec. Can. Pulp and Paper Assoc. 1936.

(54) Moelwyn-Hughes, E. A. The Kinetics of Reactions in Solution. Oxford 1933.

(55) Palmrose, C. V. Paper Trade J. 100(3): 38-39. 1935.

(56) Phillips, M. Chem. Rev. 14: 103-170. 1934.

(57) Ross. J. H., and Potter, J. C. Pulp Paper Mag. Can. 29: 569-571. 1930.

(58) St. Klein, A. Zellstoff. u. Papier. 12: 233. 1932.

(58A) Sankey, C.A., and Hibbert, H. Can. J. Research. 5: 1-47. 1931.

(59) Saunderson, H. H., Johnston, H. W., and Maass, O. ibid. 8: 415-428. 1933.

(60) Saunderson, H. H., and Maass, O. ibid. 10: 24-35. 1934.

(61) Schmidt-Nielson, S. Paper Trade J. 84(19): 43. 1927.

(62) Schörger, A. W. The Chemistry of Cellulose and Wood. McGraw-Hill Book Co., New York 1926.

(63) Stamm, A. J. J. Am. Chem. Soc. 56: 1195-1204. 1934.

(64) Stamm, A. J. J. Ind. Eng. Chem. 27: 401-406. 1935.

(65) Stamm, A. J. U.S. Dept. of Agriculture. Miscel. Pub. No. 240. 1936.

(66) Stangeland, G. E. Roy. Norwegian.Sci. Assoc. Pub. No. 1. 1932.

(67) Sutermeister, E. Chemistry of Pulp and Paper Making. Second edition. Wiley and Sons, New York 1920.

(68) Sutherland, J. W., Johnston, H. W., and Maass, O. Can. J. Research. 10: 36-72. 1934.

(69) Tomlinson, G. H. Ph. D. Thesis, McGill University 1935.

(70) Tomlinson, G. H., and Hibbert, H. J. Am. Chem. Soc. 58: 340-353. 1936.

(71) Traube, J. J. Phys. Chem. 14: 452-470. 1910.

(72) Wolensky, E. J. Ind. and Eng. Chem. 20: 1234. 1928.

(73) Yorston, F. H. Forest Products Laboratory of Canada, Montreal, Project 70M. Progress Report No. 2. 1934.

(74) Yorston, F. H. ibid. No. 3. 1935.

(75) Yorston, F. H. ibid. No. 6. 1935.

(76) Yorston, F. H. ibid. No. 10. 1936.

(77) Yorston, F. H. ibid. No. 11. 1937.

(78) Yorston, F. H. ibid. No. 12. 1937.