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Doctor's Dissertation

The Theoretical Basis for the Action of Sulfide  
in the Kraft Pulping Process

by Fred S. Hanson

June, 1939

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**THE THEORETICAL BASIS  
FOR THE ACTION OF SULFIDE  
IN THE KRAFT PULPING PROCESS**

**A thesis submitted by**

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of The Institute of Paper Chemistry for the  
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## FOREWORD

Although considerable literature exists on sulfidity effects in the kraft pulping process, there has been no clear statement of the subject and of the problems involved. Consequently it was necessary to make a fairly complete preliminary analysis and historical review of this subject.

In order to preserve a logical and orderly structure throughout this preliminary treatment, the writer's own analysis of the subject and the evidence in the literature have been considered together. This approach was found to be superior, in this particular case, from the standpoint of readability. Furthermore, in several instances an original analysis of the available data was made, and conclusions were drawn which are not actually expressed in the literature, but which cannot well be separated from this discussion without a sacrifice in the logical order of treatment.

## I. ANALYSIS OF PROBLEM AND HISTORICAL REVIEW

### A. Introduction

The active components of a kraft cooking liquor are sodium hydroxide and sodium sulfide.

The composition of a given liquor is expressed as the ratio of sodium sulfide to total active alkali on an equivalent basis:

$$\frac{\text{Na}_2\text{S (as Na}_2\text{O)}}{\text{NaOH (as Na}_2\text{O)} + \text{Na}_2\text{S (as Na}_2\text{O)}} \times 100\%$$

This value is known as the "sulfidity" of the liquor. The TAPPI definition of sulfidity expresses the denominator as "total titratable alkali." This includes sodium carbonate in addition to sodium hydroxide and sodium sulfide.

As might be expected, the proportion of sulfide, or the sulfidity, affects the cooking behavior of a kraft liquor.

### B. Effect of Sulfide

The addition of sulfide to a soda cooking liquor results in a stronger pulp and increases the rate of delignification.

The greater strength of the pulp is generally attributed to the slower rates of solution of pentosans and hemicelluloses and of degradation of the cellulose. Although the reasons for decreased action on carbohydrates and the reasons for increased action on the lignin are undoubtedly closely related, this discussion is concerned first of all with a study of the increase in rate of delignification.

The experimental evidence in the literature for the speeding up of delignification by the presence of sulfide is quite extensive.

Hawley and Wise (1) gave curves showing the removal of lignin from jack pine by a soda liquor and also by a kraft liquor made

by adding sulfur to the soda liquor. When these curves are plotted on the same graph it is seen that the delignifying action is appreciably faster with the kraft liquor. Arrhenius (2) is authority for the statement that the rate of solution of the incrustants is greater in sulfide solution and in sulfate liquor than in soda liquor of equivalent strength. Hagglund and Medlund (3) reported that an increase in the ratio of sodium sulfide to sodium hydroxide increased the pulping rate. Kress and McGregor (4) presented data for comparable kraft and soda cooks which show a lower lignin content in the kraft pulp. The data of Johansson (5) show a decrease in the chlorine number (related to lignin content) of pulps with increasing sulfidity. Considerable work has been done on this subject at the Forest Products Laboratories of Canada. The following statement is quoted from one of the publications of that institution (6): "i.e., the addition of sodium sulfide to a solution of caustic soda causes a more rapid pulping of coniferous woods." Some unpublished experiments carried out at The Institute of Paper Chemistry showed a decrease in permanganate number (related to lignin content) with increasing sulfidity.

#### C. Reason for Effect of Sulfide

A number of suggestions have been made in the literature as to why sulfide speeds up the pulping reaction. These theories, together with some additional possibilities, are discussed critically below:

1. The presence of sulfide ions may aid penetration (by raising osmotic pressure). This theory is suggested by the work of Klein (7). Actually the sulfide is present principally as hydrosulfide ions as a result of hydrolysis:



As a matter of fact, penetration is not a very important factor in alkaline cooking, because it is relatively very rapid. Furthermore, the speeding up of delignification by sulfide takes place with wood meal or wood planings as well as with chips (3).

2. "The effects of sodium sulphide are due to the maintenance of a reducing atmosphere in the digester." This is a fairly common theory which is quoted from Kress and McGregor (4). The presence of sulfide unquestionably furnishes an environment less favorable to oxidation than pure sodium hydroxide solutions. This effect could be important in preventing degradation of the cellulose. It is more difficult to understand how a reducing "atmosphere" could aid delignification. Oxidation and degradation of the lignin would seem more likely to be effective in lignin removal. There is the possibility that, in a milder "atmosphere", the lignin would be removed in larger units, which would not undergo further degradation with its consequent consumption of chemicals. This would result in a higher chemical concentration and permit more rapid pulping. This theory fails to explain studies made at the Forest Products Laboratories of Canada (5) in which the chemical concentration was maintained unchanged in all cases, and the effect of sulfide was still observed.

3. Stevens (2) has suggested that sulfide acts as a "demethylating agent". This statement is undoubtedly true. Sodium hydroxide is likewise effective as a "demethylating agent". More mercaptan is formed at high sulfidities (10), more methanol at low sulfidities (1). It is doubtful if this effect alone is responsible for increased delignification.

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4. The following theory was suggested by the writer:

"The most likely explanation for the dissolving of lignin in alkaline processes is the formation of a sodium lignate by reaction of the alkali with phenolic hydroxyl groups in the lignin. It is conceivable that, in kraft cooking, the hydroxyl groups react more readily with sodium hydrosulfide ( $\text{NaSH}$ ) than with the more stable sodium hydroxide ( $\text{NaOH}$ )."

But, as a matter of fact, sodium hydroxide and sodium hydrosulfide are essentially completely ionized in solutions of pulping strength (11). It is not immediately apparent why sodium ions should be more reactive in the presence of hydrosulfide ions than in the presence of hydroxyl ions.

5. There is a possibility that sodium sulfide acts catalytically in kraft cooking.

It is difficult to conceive of any catalytic mechanism other than a possible reaction of hydrosulfide ion with the lignin to replace hydroxyl groups. The  $-\text{SH}$  groups thus formed could react with sodium ion to give  $-\text{SNa}$  groups.

6. There is evidence in the literature that the more rapid action of kraft cooking liquors depends on the formation of sulfur groups in the lignin molecule, and that these groups render the lignin more soluble.

Denisov (12) quotes Klasen to the effect that most of the sulfur in the cooking liquor "goes from the  $\text{NaSH}$  into a combined state with the lignin acids and other organic substances. Furthermore the  $\text{SH}^-$  group enters preferentially into reaction with the wood, and thereafter the sodium sulfide behaves itself just like  $\text{NaOH}$ ." Klasen



concludes from this that sodium sulfide is twice as weak as sodium hydroxide.

Klason gives ample data to show that sulfur does combine with the lignin. He has made sulfur balances on kraft cooks (12, 13) which show 40 - 50 per cent of the sulfur combined with the lignin in the black liquor.

Hausser (14) found that only 7 - 15 per cent of the sodium sulfide in the liquor was consumed in kraft pulping, but his study was made with beechwood. This discussion is concerned primarily with the kraft pulping of coniferous woods.

Kullgren (15) has made considerable progress in this field. Since the hydrolysis of sodium sulfide is so nearly complete at room temperature, he concluded that, in a kraft cooking liquor, only sodium hydroxide and sodium hydrosulfide are present at cooking temperatures. Kullgren digested wood with pure sodium hydrosulfide, and in none of his experiments did he obtain a yield lower than 70 per cent. Digestions of wood with sodium hydroxide produced the same yield in a shorter time with weaker cooking liquors. However, when both these products were digested with sodium hydroxide, it was found that the chips which had been precooked with sodium hydrosulfide pulped considerably faster. (An analysis of Kullgren's data shows that, the higher the sulfur content of the chips obtained in the sodium hydrosulfide cooks, the more rapid the subsequent digestion.) Kullgren's conclusions contain the following statement: "This behavior of sulfide in kraft cooking depends on the fact that  $\text{NaSH}$ , which itself is a weak digestion medium, forms sulfur compounds which are more easily attacked by the soda liquor than the sulfur-free substance."

\* \* \* \* \*

From the above survey it may be concluded that the speeding up of the pulping reaction by sodium sulfide is due, very probably, to the action of sodium hydrosulfide on lignin.

#### D. Optimum Sulfidity

A number of investigators have reported that the increase of pulping rate with increasing sulfide content does not hold over the whole range of sulfidities. An increase in the percentage of sulfide above a certain value resulted in an ultimate decrease in pulping rate. In other words, it was found that, under the conditions of the experiments in question, there was an optimum sulfidity for maximum delignification rate.

Hagglund and Hedlund (3) found that delignification was only slightly better at 31 per cent sulfidity than at 15.6 per cent. They concluded that it is not advantageous to go higher than 15.6 per cent. Krens and McGregor (4) reported that delignification was at a maximum and the best pulp was produced at a sulfidity of 33.5 per cent. This has been confirmed by unpublished work carried out recently at The Institute of Paper Chemistry. Johansson's results (5) indicated that maximum delignification occurred between 25 and 50 per cent sulfidity. An extensive study of sulfidity at the Forest Products Laboratories of Canada led Mitchell and Rees (6) to make the following statement:

"It is a generally accepted view that whereas the addition of sodium sulphide to a solution of caustic soda causes a more rapid pulping of coniferous woods, the substitution of sodium sulphide for more than a certain proportion of the caustic soda in the pulping liquor leads to a diminution of the pulping power of the liquor. This

is only true where the conditions of the experiment are mainly substantially close to those now used in commercial practice."

### E. Reason for Optimum Sulfidity

Although no good explanation for the occurrence of an optimum sulfidity is available in the literature, the writer found that a systematic analysis of the available data revealed some interesting facts.

The data of Magglund and Hedlund (5), Kress and McGregor (4), Surface and Cooper (16, 17), Bray and Curran (18), Johansson (9), and Klason (10) were calculated to a comparable basis. The total chemical content of the cooking liquor was expressed in terms of sodium hydroxide and sulfidity was expressed according to the TAPPI definition. A calculation was made of the total sodium hydroxide present in each cook, including the sodium hydroxide obtained by complete hydrolysis of the sodium sulfide. This term was designated as "effectual NaOH".

A study of these figures showed an approximate agreement among the results of all the investigators as to the minimum amount of "effectual NaOH" which was required for effective pulping. Table I summarizes this result.

The minimum value of "effectual NaOH" which resulted in complete pulping is thus seen to be in the neighborhood of 12 per cent, calculated as  $\text{Na}_2\text{O}$  -- or between 15 and 16 per cent, calculated as NaOH.

This is a very interesting fact. No investigator has pulped wood successfully with a kraft liquor containing less than this critical minimum of effectual NaOH. The result obviously holds

for the total chemical range of 19.7 to 27.5 per cent as indicated in Table I. It is concordant with the requirement of a definite quantity of sodium hydroxide that Johansson and Klason, who used higher percentages of total chemical, were able to pulp at higher sulfidities than the other investigators. For, obviously, when more chemical is used, the minimum amount of sodium hydroxide is present at higher sulfidities.

TABLE I  
MINIMUM EFFECTUAL HYDROXIDE

Investigators	Minimum Effectual NaOH (as Na O) for Good Pulping (%)	Sulfidity %	Total Chemical %
Hagglund & Hedlund	15.68*	31	24.0
Bray & Curran	12.97	33	20.2
Kress & McGregor	12.45	40	20.2
Institute data	11.63	50	20.0
Surface & Cooper	12.35	60	19.7
Johansson	12.95	75	26.7
Johansson	(11.35)**	(90)	(26.7)
Klason	12.25	85	27.5

\*Lowest value investigated.

\*\*Not quite effective.

Mitchell (6), at the Forest Products Laboratories of Canada, was aware of this principle when he made the statement that the diminution of the pulping power of kraft liquors at high sulfidities is observed "only when the conditions of the experiment are mainly substantially close to those now used in commercial practise." He pointed out that Kress and McGregor obtained poor delignification at high sulfidities because they worked at a fixed

total chemical of 20 per cent, and that consequently, at the higher sulfidities, there was insufficient alkalinity present. Working with a large excess of chemical, Mitchell pulped successfully at 100 per cent sulfidity -- in fact at a much faster rate than in a comparable solution of 55 per cent sulfidity. His results will be discussed in detail in the next section.

The following conclusion may be drawn from the above discussion:

With limited total chemical, more than a certain sulfide content results in an ultimate decrease in pulping power, apparently because of a lack of sufficient sodium hydroxide.

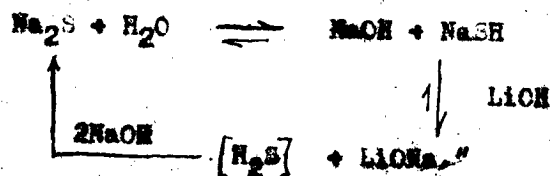
There are a number of possible explanations for this requisite minimum of effectual NaOH in kraft cooking.

1. The statement is still occasionally made that "caustic is the only real pulping agent".
2. The presence of hydroxyl ions may be necessary to degrade the lignin molecule and to bring about its diffusion into the liquor, or they may be necessary for the hydrolysis of the "lignin-carbohydrate" bonds.

This seems possible at this point. There is little concrete evidence in the literature either to support or detract from this statement. Mitchell's results (6), which will be presented below, show a parallel removal of lignin and carbohydrate by various kraft liquors.

3. The following theory was suggested by the writer in a report on some unpublished work carried out at The Institute of Paper Chemistry:

"It may be that a reaction of sodium hydrosulfide with lignin to form sodium lignate can only occur in the presence of excess sodium hydroxide which removes the hydrogen sulfide formed:



This mechanism does not seem too likely when we consider that sodium hydrosulfide is actually present as sodium ion and hydrosulfide ion. The reaction forming sodium lignate is probably with the sodium ion, which can come equally well from sodium hydroxide or sodium hydrosulfide.

4. Results obtained at the Forest Products Laboratories of Canada (6) suggest that excess alkalinity is required at the end of the cook to keep lignin bodies in solution. The statement was made that "the acidic compounds formed in the pulping of spruce consume approximately from 12 to 14 grams of caustic soda per hundred grams of wood as computed from solutions titrated to the phenolphthalein change point. If the solution becomes more acid than pH 9, lignin bodies have a tendency to become alkali insoluble."

This seems entirely plausible.

However, the only permissible statement at this point is that there appear to be reactions in the kraft cook requiring the presence of a definite amount of hydroxyl ion.

#### F. Results with Excess Sodium Hydroxide

The falling off of pulping rate at high sulfidities because of insufficient hydroxide does not explain results obtained at the

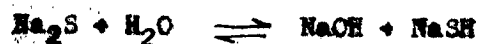
Forest Products Laboratories of Canada (6), where a very large excess of chemical was used and optimum effects were still observed.

The liquor volume used was sufficiently large so that the concentration of chemical was not changed by more than 15 per cent during the cook, even in the weakest solutions studied. With solutions of 1.0 per cent concentration it was found that delignification was progressively more complete as the sulfidity was increased to 50 per cent, beyond which point an increase in the proportion of sulfide caused no change in the lignin content of the pulp or in the yield. At concentrations of 1.5, 2.0, and 3.0 per cent a fairly definite optimum was observed at 50 per cent sulfidity. Further studies (12) with large volumes of chemical at 1 per cent concentration showed that, under these conditions, a liquor of 100 per cent sulfidity is definitely superior to a liquor of 55 per cent sulfidity.

Thus it is indicated, by these results, that delignification rate does not continue to increase with increasing sulfidity, even in the presence of excess sodium hydroxide, except perhaps in quite dilute solutions.

#### G. Possibility of Hydrolysis Effect

If the behavior of sulfide solutions is different in dilute solutions, as the above results suggest, then the difference might be traceable to a variation in the degree of hydrolysis of sodium sulfide with a change in concentration:



It has been seen that sodium hydroxide and sodium hydrosulfide appear to be the active components of the liquor. If this

hydrolysis were complete or nearly complete in dilute solutions at cooking temperatures, the same number of mols of the active components would be available at all sulfidities. However, if in more concentrated solutions hydrolysis were not complete, fewer mols of the active components would be initially available at high sulfidities and an optimum in delignification rate might be observed.

The extent to which sodium sulfide is hydrolyzed at cooking temperatures is not known. The available data (11) indicate that the hydrolysis is from 60 to 90 per cent complete at room temperatures and is naturally subject to changes in concentration.

The only direct available evidence of possible incomplete hydrolysis of sodium sulfide at cooking temperatures is the work, mentioned above, of the Forest Products Laboratories of Canada. Opposed to this there are indications, in other studies made at the same institution, that the degree of hydrolysis of sodium sulfide does not change with concentration at cooking temperatures.

These contrary indications appear in some very excellent studies of the kinetics of the soda and kraft pulping processes (8, 20). The reaction rate constants, which were obtained for the main delignification reaction with pure sodium sulfide, increase linearly with an increase in the concentration of sodium sulfide in the range studied (0 - 6 per cent solutions). This implies that there was no change in the degree of hydrolysis of sodium sulfide with change in concentration.

#### II. Conclusions

A study of the literature thus leads us to the following conception of the action of sulfide in the kraft pulping process:



Sodium sulfide speeds up alkaline pulping, a result very probably of the action of sodium hydrosulfide on lignin. With limited total chemical, more than a certain sulfide content results in an ultimate decrease in pulping power, apparently because of a lack of sufficient sodium hydroxide.

Although the evidence is not conclusive, it is possible that, even in the presence of excess sodium hydroxide, delignification rate does not continue to increase with increasing sulfidity, except perhaps in quite dilute solutions. If this is the case, the explanation may well involve a determination of the degree of hydrolysis of sodium sulfide under cooking conditions.

## II. EXPERIMENTAL WORK AND DISCUSSION OF RESULTS

### A. Effect of Concentration on Optimum Sulfidity

Three series of pulping experiments were made to determine the relative delignifying powers of kraft liquors of different sulfidities when sufficient sodium hydroxide is present. These series of digestions were made with chemical concentrations of 1, 3, and 6 per cent. A ratio of 50 per cent total chemical was chosen so that the amount of sodium hydroxide present would exceed a minimum value of 16 per cent at the highest sulfidity studied. The chemical was calculated in terms of sodium hydroxide and was based on the oven-dry weight of the wood.

### Experimental Procedure

A prime stick of black spruce was barked with a drawknife and reduced to shavings with a handplane. The shavings were thoroughly mixed on a one-fourth inch screen and sampled for moisture. A sealed glass jar was used for storage.

The cooking liquors were made up with c.p. sodium hydroxide, c.p. sodium hydrosulfide, and distilled water. The solutions of sodium hydroxide and sodium hydrosulfide were made up and titrated separately and then mixed in the proper proportions for each cook. Titration of the sodium hydroxide was made with 0.5 N hydrochloric acid to the methyl orange end point. Excess 0.5 N sulfuric acid was added to a sample of the sodium hydrosulfide solution and all the hydrogen sulfide was boiled out as shown by a test with lead acetate paper. The solution was then cooled and the excess acid was titrated with 0.2 N sodium hydroxide.

A stainless steel autoclave of about five liters capacity was used for the digestions. The autoclave was heated in a wax bath by means of four gas burners.

Ninety grams of shavings (on the oven-dry basis) were used for each cook. In the case of the 3 and 6 per cent cooks it was necessary to alternately moisten the shavings and tamp them firmly into the digester; otherwise the volume of liquor used would not have sufficed to cover the wood. A lead weight was placed on top of the shavings in these two series of cooks.

An arbitrary cooking time was chosen for each concentration of cooking liquor used. The temperature was merely recorded for the first

cook at each concentration. Each succeeding cook at that concentration was held to the temperature schedule obtained from the first cook. The pressure was also recorded. (It did not differ from steam pressure even when the cooking liquor contained excess sodium hydrosulfide.) The digester was removed momentarily from the wax bath and relieved to zero pressure at 102 - 105° C. At the end of the cook the pressure was relieved to zero as rapidly as possible.

The product was washed in the digester and on a Buchner funnel (using a filter cloth) with successive 2-liter portions of cold tap water until the filtrate was colorless. About 14 liters of water were required in most cases. The filter cloth containing the pulp was then squeezed as dry as possible by hand (about 25 per cent dry) and the product was weighed and sampled for moisture.

At first both permanganate number and lignin determinations were run on the product. The permanganate number determination did not prove to be entirely satisfactory, because the reagent did not react completely with the shives from a very raw cook, even when the pulp was disintegrated. The permanganate number determination was consequently discontinued. Lignin was determined according to Institute Method 15. The oven-dry sample was disintegrated in a Costa Hall disintegrator. The filtration was made on a Gooch crucible. A weighed amount of acid-washed, oven-dry asbestos (about 0.2 gram) was added to each lignin sample, as a filter aid, just before filtration.

The data for these pulping studies are presented in Table II.

TABLE II  
EFFECT OF CONCENTRATION ON OPTICAL MULTIPLICITY

Digestions at 1% Concentration

Liquor volume 4500 cc.

1 hour to 170° C., 2 hours 35 minutes at 170° C.

Sulfidity %	Parts NaOH	Parts NaSH	Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohydrate %
0	50.0	0	60.29	25.88	14.38	45.82
33	41.7	8.3	60.80	23.58	14.34	46.46
60	35.0	15.0	60.47	22.76	13.77	46.70
100	25.0	25.0	53.45	19.40	10.37	43.08
120	20.0	30.0	59.55	21.65	12.90	46.65

TABLE II (Continued)

## EFFECT OF CONCENTRATION OF OPTIMUM SULFIDITY

Digestions at 3% Concentration

Liquor volume 1500 cc.

44 minutes to 170° C., 65 minutes at 170° C.

Sulfidity %	Parts NaOH	Parts NaSH	Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohydrate %
0	50.0	0	60.10	29.40	15.27	44.83
33	41.7	8.3	49.60	10.60	5.26	44.34
60	35.0	15.0	49.50	10.10	4.98	44.52
100	25.0	25.0	47.50	6.20	2.95	44.55
120	20.0	30.0	48.55	7.21	3.50	45.05

Digestions at 6% Concentration

Liquor volume 750 cc.

36 minutes to 170° C., 40 minutes at 170° C.

Sulfidity %	Parts NaOH	Parts NaSH	Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohydrate %
0	50.0	0	52.60	15.43	8.13	44.47
33	41.7	8.3	51.60	14.04	7.27	44.53
60	35.0	15.0	50.90	13.68	6.96	45.94
100	25.0	25.0	51.60	13.27	6.85	44.75
120	20.0	30.0	53.03	12.96	6.87	46.16

In the above table "residual lignin" is the percentage of lignin remaining in the pulp on the basis of the original wood, and "residual carbohydrate" is the value obtained by subtracting the residual lignin from the yield.

The values for residual lignin show the relative degrees of cooking obtained at the various sulfidities. It will be observed that the residual lignin decreased with increasing sulfidity up to 100 per

cent, where an optimum was obtained. This held true for all three concentrations studied. There is no apparent evidence of a decrease in optimum sulfidity with increasing concentration as the result of a possible decrease in the hydrolysis of the sodium sulfide.

In other words, the following conclusions may be drawn from these data:

First. An optimum sulfidity was observed even in the presence of excess sodium hydroxide.

Second. The numerical value of the optimum sulfidity did not change with concentration (in the range 1 - 6 per cent).

Third. The fact that the optimum sulfidity did not change with concentration is good evidence that the degree of hydrolysis of sodium sulfide did not change with concentration and hence must be virtually complete at cooking temperatures.

It may be mentioned that the pulps obtained with 6 per cent solutions were not as uniformly cooked as those obtained with the weaker cooking liquors. This result may be ascribed, in part, to the necessity for packing the shavings tightly into the bottom of the digester so that they would be covered by the small volume of liquor used. The shavings in direct contact with the bottom of the digester were always somewhat overcooked. The effect of nonuniformity is furthermore inherent in the use of concentrated liquors and a short cooking time.

It will be observed that the data for residual carbohydrate material are, in general, quite uniform. This is in accord with results obtained at the Forest Products Laboratories of Canada (6). The action of the soda liquors does not appear to have been more drastic than that of the kraft liquors. A more drastic action would result if an attempt

were made to delignify the wood as thoroughly with the soda liquors as is possible with the kraft liquors.

### B. Effect of Total Chemical on Optimum Sulfidity

In the previous section the optimum sulfidity for delignification was found to be 100 per cent (pure sodium sulfide) when the total chemical used was 50 per cent. It was considered desirable to find out whether an optimum at 100 per cent sulfidity is characteristic in all cases where an excess of sodium hydroxide is present. With this purpose in mind digestions were made at sulfidities of 100 and 120 per cent, using 65 per cent total chemical.

### Experimental Procedure

The cooking procedure was essentially the same as that described in the previous section. Improvements in technique were made through the use of a porcelain desiccator plate between the bottom of the digester and the bottom of the wax bath to prevent local overheating, and the use of an iron weight in place of a lead weight on top of the shavings. Iron is more resistant to alkaline cooking liquors.

The data obtained follow.

TABLE III  
COMPARISON OF DELIGNIFYING POWER AT  
SIXTY-FIVE PER CENT TOTAL CHEMICAL

65 per cent total chemical, 5 per cent concentration  
48 minutes to 170° C., 60 minutes at 170° C.

Cook	Sulfidity %	Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohy- drate %
65AR	100	50.90	6.40	3.26	47.64
65BR	120	48.50	4.97	2.41	46.09

Thus at 63 per cent total chemical a liquor containing excess sodium hydrosulfide was found to be more effective than pure sodium sulfide.

For the sake of completeness, and to see how the optimum varied with total chemical over the whole range, the following cooks were made:

TABLE IV

EFFECT OF TOTAL CHEMICAL ON OPTIMUM SULFIDITY

40 per cent total chemical, 3 per cent concentration  
62 minutes to 170° C., 65 minutes at 170° C.

Cook	Sulfidity %	Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohy- drate %
16	70	51.35	7.42	3.81	47.54
17	80	51.79	7.08	3.66	48.04
18	90	50.54	8.63	4.34	46.00
19	100	54.00	11.04	5.96	48.04

35 per cent total chemical, 3 per cent concentration  
60 minutes to 170° C., 70 minutes at 170° C.

Cook	Sulfidity %	Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohy- drate %
23	50	49.80	7.44	3.71	46.09
20	60	49.95	7.03	3.51	46.44
21	70	49.75	6.51	3.24	46.51
22	80	52.10	8.89	4.63	47.47

With 40 per cent total chemical the optimum occurred at 80 per cent sulfidity and with 35 per cent total chemical the optimum was at 70 per cent sulfidity.

The following table contains the data which are now available on the relationship between total chemical and optimum sulfidity:

TABLE V

DEPENDENCE OF OPTIMUM SULFIDITY ON TOTAL CHEMICAL

Total Chemical	Optimum Sulfidity
20.0	33 Kress & McGregor (4)
26.7	50 Johansson (5)
35.0	70
40.0	80
50.0	100
65.0	120 partial data only

These data are represented graphically in Figure 1.

Apparently the optimum sulfidity increases regularly with the amount of total chemical used. Figure 1 indicates the most desirable sulfidity when operating with any given amount of total chemical. Commercially the sulfidity of a kraft liquor is limited by the efficiency of the soda recovery -- the higher the efficiency, the lower the sulfidity. Moreover, the total chemical used is limited by economic considerations to the range 18 - 28 per cent. The results indicate that sulfidities slightly higher than those generally obtained should be quite effective in this range.\*

\*A method might be worked out for increasing the sulfidity of kraft liquors in the mill. But, because the superior effectiveness of high sulfidity liquors is tied up with the use of a high total chemical ratio, it does not appear advisable to do so. Such a method might depend upon heating iron and sulfur, treating with hydrochloric acid, and passing the evolved hydrogen sulfide into the liquor after causticizing. The ferrous chloride, treated with chlorine (or with air), would give ferric chloride, which on heating gives three molecules of hydrochloric acid, and a residue of ferric oxide.



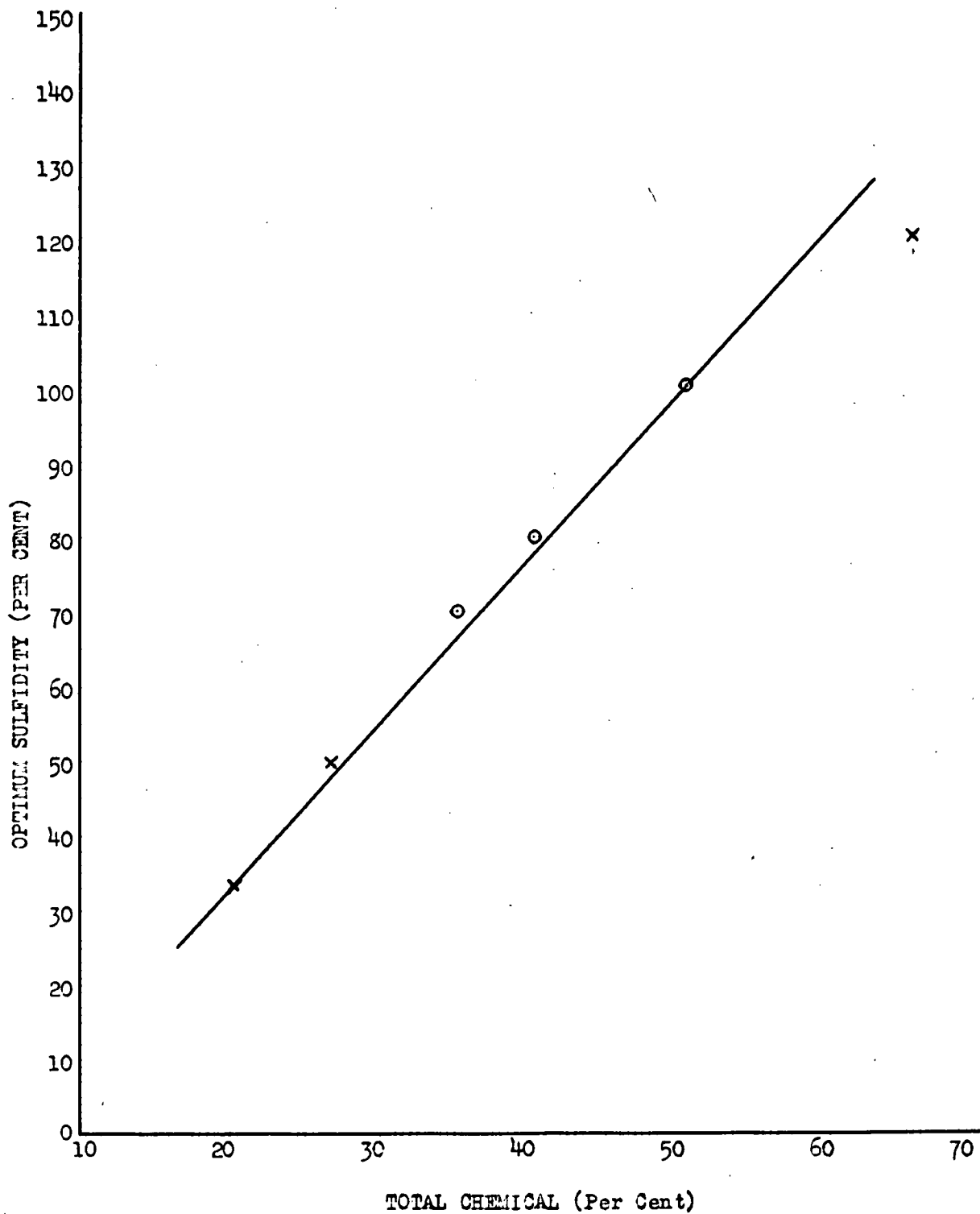


FIGURE 1. THE RELATIONSHIP BETWEEN TOTAL CHEMICAL AND OPTIMUM SULFIDITY IN THE KRAFT PULPING PROCESS.

## C. Pulping Behavior of Sodium Hydrosulfide

### 1. Preliminary Studies

It was decided to extend the work of Kullgren (15) by making a further study of the action of pure sodium hydrosulfide on wood.

In the first experiments six digestions were carried out using pure sodium hydrosulfide as the pulping agent. Digestions were made with 20, 30, and 40 per cent total chemical (calculated as sodium hydroxide) for 3 hours at 160° C., and with 20, 25, and 30 per cent total chemical for 4 hours at 160° C.

### Experimental Procedure

The digestions were made three at a time in three iron tubes contained in the digester previously described.

TABLE VI

#### SIMULTANEOUS DIGESTIONS WITH HYDROSULFIDE

Cook	Total Chemical %	Time at 160° C.
31	20	3
32	30	3
33	40	3
34	20	4
35	25	4
36	30	4

Cooks 31, 32, and 33 were made simultaneously; a second series of cooks (34, 35, and 36) was likewise made simultaneously. Fert/ grams of spruce

planings (on the oven-dry basis) were used for each cook. The liquor volume was 400 cc. in each case; therefore the concentrations were 2, 3, and 4 per cent in Cooks 31, 32, and 33 respectively, and 2, 2.5, and 3 per cent in Cooks 34, 35, and 36. The space surrounding the tubes was half filled with a liquor of average concentration. During the course of the cook the relative volumes in the tubes changed slightly. This means that the concentrations of the weaker liquors increased somewhat, whereas the concentrations of the stronger liquors decreased. However, the total chemical, which, as will be seen below, is the important item in this particular case, remained unchanged.

The pH values of the cooking liquors before and after the digestion were determined, as a matter of possible interest, by means of a standard glass electrode, calibrated at pH 3.38 with sodium acid phthalate.

The yield and the lignin content of the pulps were determined. The dissolved lignin in the black liquor was precipitated and purified according to the method of Marshall (21) as follows:\*

The black liquor was filtered to remove fiber and iron sulfide. The alkali lignin was precipitated with concentrated hydrochloric acid until the solution was acid to litmus paper; a slight excess of hydrochloric acid was then added. The precipitate was centrifuged and washed with saturated sodium chloride solution until acid-free to litmus paper. The precipitate was then drained as dry as possible on a Buchner funnel and dissolved in dioxane. The solution was dehydrated as completely as possible with a mixture of equal parts of magnesium sulfate and sodium sulfate; this required a double treatment with about 15 grams of the mixture each time. The solution was then concentrated to 125 - 150 cc. and precipitated dropwise into 1200 - 1500 cc. of absolute ether. The precipitate was centrifuged, washed with ether, twice with carbon disulfide, again with ether, and finally with petroleum ether, using the centrifuge throughout as a means of separation.

The methoxyl content of this alkali lignin was determined according to the semimicro method of Leisl. The sulfur content was determined by the Carius method. The ash content was likewise determined. The sulfur content of the pulps was determined according to a procedure recently described by Klingstedt (22).

The results of the above investigations will be found in Table VII.

\*The product obtained by this method is called Alkali Lignin A, and represents the principal fraction of the lignin least modified by the cooking process.

TABLE VII

## DIGESTION OF SPRUCEWOOD WITH SODIUM HYDROSULFIDE

All cooks at 160° C., 65 minutes to maximum temperature, 400 cc. volume.

Cook	Total Chem-ical %	Concn. %	Time at Max. Temp. hr.	pH White Liq. vor	pH Black Liq. vor	Yield %	Lignin in Pulp %	Resid-ual Lignin %	Carbo-nyl Grate %	MeO in Alkali Lignin %	Ash in Alkali Lignin %	S in Alkali Lignin %	S Groups in Alkali Lignin	S in Pulp %	S in Lignin in Pulp
31	20	2	3	11.57	10.54	64.80	22.29	14.44	50.36	13.19	2.23	6.05	1.7	0.402	1.80
34	20	2	4	11.57	10.55	65.10	22.47	14.63	50.47	11.67	1.81	7.79	2.2	0.416	1.85
35	25	2.5	4	11.50	10.94	58.94	17.76	10.47	48.47	13.13	2.59	7.59	2.1	0.259	1.46
32	30	3	3	11.43	11.13	54.50	12.60	6.86	47.64	13.36	0.52	6.80	1.9	0.206	1.64
36	30	3	4	11.43	11.15	54.90	13.12	7.20	47.70	12.40	2.50	7.64	2.1	0.257	1.96
33	40	4	3	11.30	11.19	50.60	5.77	2.92	47.68	13.12	2.04	10.72	3.0	0.178	3.08

\* Corrected for ash content.

The sodium hydrosulfide cooks were characterized by a peculiar odor which is different from the usual mercaptan odor of kraft cooks.

The product obtained in Cook 33 was fully pulped. When the pulp was first washed it was dark gray-green in color, but on standing it soon turned to a red-brown. It appeared to be a good strong pulp as might be expected from the high figure for residual carbohydrate.

The alkali lignins, with the exception of that from Cook 34, were a very light brown. The product from Cook 34 was somewhat darker than the rest. The appearance of these products was quite similar to that of the product which may be obtained by dissolving Willstatter lignin in pure sodium sulfide and precipitating with acid.

From the results of the above work, as presented in Table VII, the following conclusions are indicated:

First. It is possible to pulp wood completely with sodium hydrosulfide.

Second. The amount of total chemical required in the pulping of wood with sodium hydrosulfide is in the neighborhood of 40 per cent (calculated as sodium hydroxide). This result is not completely proved by the above results, and further work on this point will be presented in the next section. Discussion of the significance of this result is reserved until then.

Third. The pulping action of sodium hydrosulfide involves the introduction of sulfur atoms into the lignin molecule.

The number of sulfur atoms, corresponding to the percentages of sulfur in the alkali lignin products obtained in the above experiments, was calculated on the basis of a molecular weight for lignin of 860 as given by Brauns and Hibbert (23). The result is given in Table VII.

The methoxyl content of the various alkali lignin products was roughly the same in all cases. The low value observed in Cook 34 is in accord with the off-color product obtained.

The sulfur content of the alkali lignin and of the pulp increased with concentration and with time. Apparently after the lignin is removed it may still be acted upon by the liquor, as indicated in Cooks 34 and 36.

The pH of the white liquors used was about 11. The pH of the black liquors indicates that the sodium hydrosulfide was relatively further exhausted in Cooks 31, 34, and 35 than in Cooks 32, 36, and 33.

## 2. Confirmation of Total Chemical Requirement

The following experiments were made to obtain further evidence concerning the amount of sodium hydrosulfide required to produce a commercial pulp.

### Experimental Procedure

Four cooks were made simultaneously, as described previously, using 30, 35, 40, and 45 per cent of sodium hydrosulfide. All four cooks were made at 3.8 per cent concentration so that there would be little change in the relative liquor volumes in the four containers. A maximum temperature of 170° C. was employed, and the cooks were held at this temperature for a relatively long period of time to allow the liquors to approach exhaustion. The schedule used was 1 hour, 10 minutes to maximum temperature, and 8 hours at maximum temperature.

The data obtained from these cooking studies are presented in Table VIII.

The most important conclusion to be drawn from these data is that more than 35 per cent of sodium hydrosulfide is required to produce a pulp in the commercial range. The pulp obtained with 40 per cent hydrosulfide was quite thoroughly delignified. The value 40 per cent for hydrosulfide appears to be approximately equivalent to the value

TABLE VIII

## AMOUNT OF HYDROSULFIDE REQUIRED FOR COMPLETE PULPING

All cooks at 3.6 per cent concentration.

pH of white liquors 11.33.

1 hour 10 minutes to 170° C., 8 hours at 170° C.

Cook	NaSH %	Volume cc.	pH Black Liquor	Yield %	Residual Lignin %	Residual Carbo-hydrate %	3 in Alkali Lignin %	3 in Alkali Lignin %	3 in Pulp % of Lignin in Pulp	
41	30	300	10.94	55.20	21.51	11.87	43.33	5.26	1.5	-
42	35	350	11.08	45.65	8.90	4.06	41.59	5.52	1.6	-
43	40	400	11.16	40.00	2.68	1.07	38.93	5.12	1.5	5.67
44	45	450	11.08	36.95	1.85	0.68	36.27	4.82	1.3	12.76

20 per cent for sodium hydroxide. It will be recalled that, in the case of Cook 33, a pulp containing 5.7 per cent lignin was obtained with 40 per cent of sodium hydrosulfide in 3 hours at 160° C.

The successful pulping of wood with sodium hydrosulfide makes it necessary to discard the previous conclusion (part I, section E) that a definite minimum of hydroxide is necessary in order to pulp wood completely with sulfide solutions. It now appears that the reason for the decrease in pulping power at high sulfidities, at constant total chemical, is the requirement of a higher total chemical as the hydrosulfide component is increased. For, if the use of pure sodium hydroxide requires 20 per cent chemical, while the use of pure sodium hydrosulfide requires 40 per cent chemical, then, as sulfidity is increased at constant total chemical, the effective total chemical is decreased. The minimum of sodium hydroxide which appeared necessary in the preliminary analysis of this subject is the natural consequence of these facts in the total chemical range of 20 - 27 per cent, which was the range covered by the data previously available. Another consequence of this fact is that the minimum amount of chemical required to pulp wood at a given sulfidity increases with the sulfidity. Partial data on this latter relationship are available in the literature:

TABLE II

## MINIMUM CHEMICAL REQUIREMENT AT VARIOUS SULFIDITIES

Sulfidity %	Minimum Total Chemical For Effective Pulping %	Investigators
40	20.2	Kress & McGregor (4)
50	20.0	The Institute of Paper Chemistry
85	27.5	Klaason (10)
90	26.7	Johansson (2)



These data, together with the value of 40 per cent for pure sodium hydrosulfide, are plotted in Figure 2. The increase of the optimum sulfidity with an increase in the total chemical used is likewise a consequence of this same relationship. For, as the total chemical is increased, the point where the minimum amount of chemical is approached occurs at higher sulfidities.

It is not readily apparent why the pulping of wood with sodium hydrosulfide alone requires the use of 40 per cent chemical. The answer probably lies in the behavior of sodium hydrosulfide as a base when it combines with the various organic acids formed during the cooking process, rather than in the reaction whereby sulfur is added to the lignin. The maximum amount of sulfur combined with the lignin in the present experiments was 10.72 per cent in Cook 33, and this corresponds to only about 4.5 per cent sodium hydrosulfide on the weight of the wood.

In Table VIII the sulfur content of the alkali lignin products is somewhat lower than that obtained in the first experiments with sodium hydrosulfide. It is probable that the higher temperature or extremely long cooking time employed is responsible for this. It is also indicated in Table VIII that an increase of concentration under these conditions can decrease the sulfur content of the lignin product.

### 3. Pulping of Chips

The above studies with sodium hydrosulfide were made with spruce shavings. One hydrosulfide cook was carried out using chips. The wood in this case was southern pine. The conditions were chosen from the above experiments as being ideal for the production of a well cooked pulp. The data are given in Table IX.

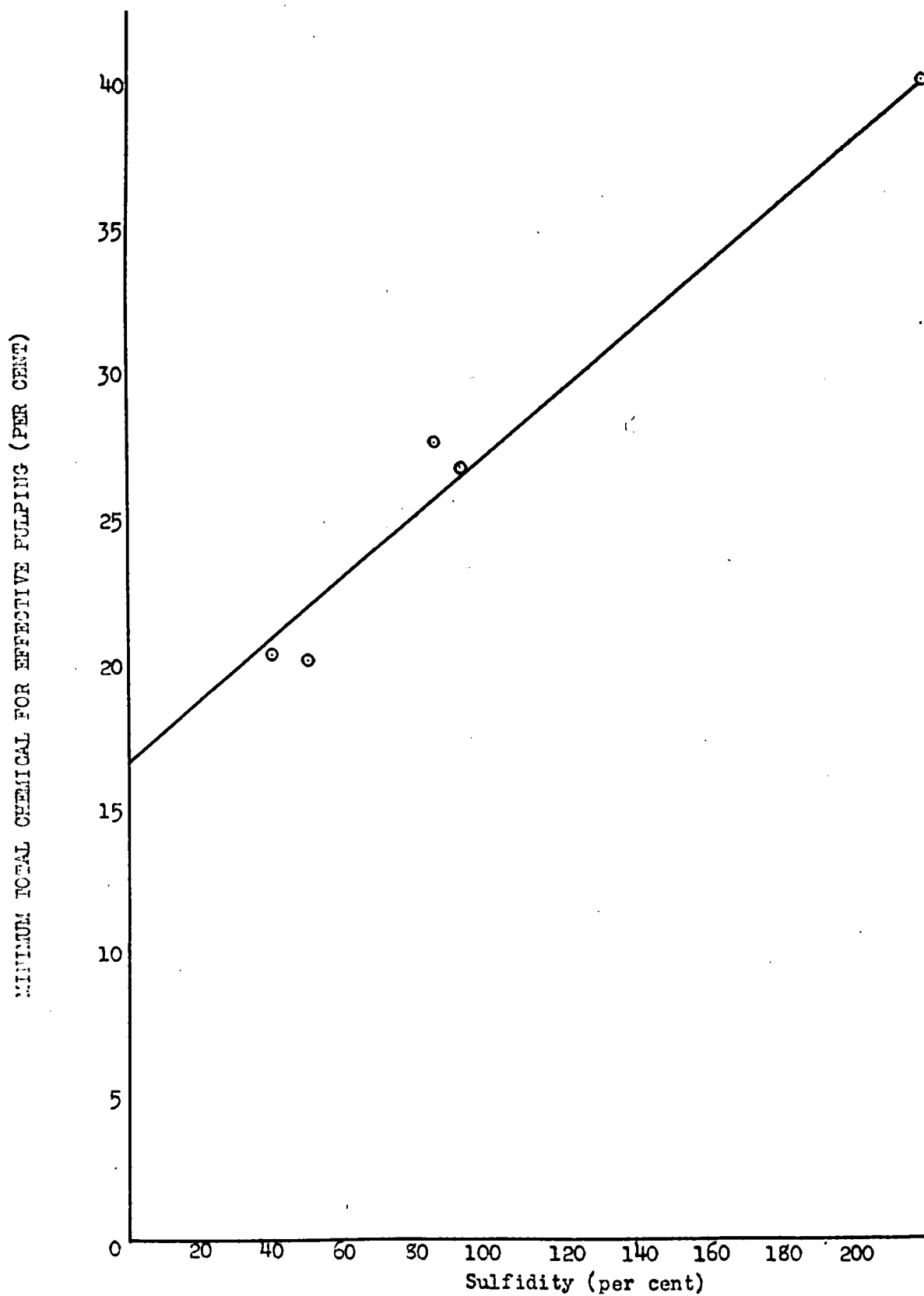


FIGURE 2. THE MINIMUM AMOUNT OF CHEMICAL NECESSARY FOR EFFECTIVE PULPING AT VARIOUS SULFIDITIES.

TABLE X

## PULPING OF CHIPS WITH HYDROSULFIDE

Weight of wood grams	Liquor Volume cc.	Total Chemical %	Time to 165° C.	Time at 165° C.	Pulp Yield %	Screen- ings %	Lignin %
500	3000	40	1 hr.	3½ hr.	44.30	1.17	3.11

The results show that the pulping behavior of hydrosulfide is as satisfactory with chips as it is with planings.

D. Effect of Sulfidity on Sulfur Content of Lignin Removed

Four cooks with liquors of varying composition were made simultaneously. Liquors containing 25, 50, 75, and 100 per cent sodium hydrosulfide were used, the other component being sodium hydroxide.

The data for these digestions are presented in Table XI.

The alkali lignin products from these cooks were purified with extreme care. The sulfur contents of these lignin products are plotted against the sodium hydrosulfide contents of the liquor in Figure 3.

It may be mentioned that the alkali lignin product obtained at 25 per cent sodium hydrosulfide was darker than the rest and that the yield of this product was less.

Figure 3 shows that the sulfur content of the dissolved lignin increased directly at first with an increase in the sodium hydrosulfide content of the liquor; it approached a limiting value of approximately 10 per cent.

The following mechanism was suggested (part I, section E) as a possible explanation of the rapid action of kraft liquors.

TABLE XI

EFFECT OF LIQUOR COMPOSITION ON SULFUR CONTENT OF LIGNIN

Conditions for all cooks:

3 per cent concentration      30 per cent total chemical  
40 grams wood              400 cc. liquor  
1 hour to 170° C.              1-1/2 hour at 170° C.

Cook No.	NaOH %	NaHS %	Yield %	Lignin %	Residual Lignin %	Residual Carbo-hydrate %	3 in Alkali Lignin %	3 in Pulp %	3 in Pulp % of Lignin in Pulp
51	75	25	47.95	6.93	3.33	44.62	6.10	0.187	2.70
52	50	50	49.60	7.13	3.54	46.05	8.85	0.255	3.60
53	25	75	50.70	9.59	4.86	45.84	9.38	0.348	3.60
54	0	100	53.10	11.00	5.84	47.26	9.88	0.385	3.50

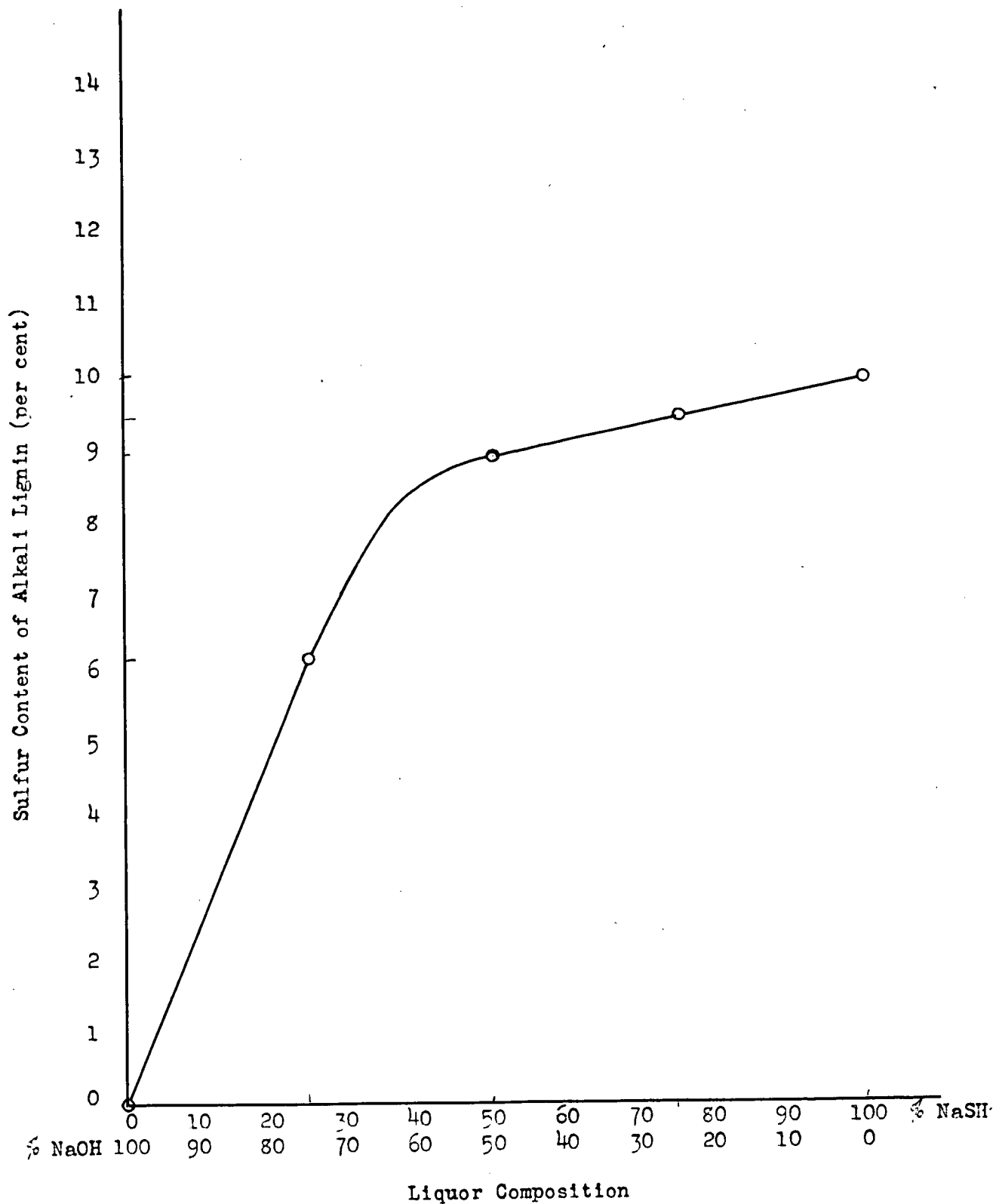


FIGURE 3. The Effect of Liquor Composition on the Sulfur Content of the Lignin Dissolved

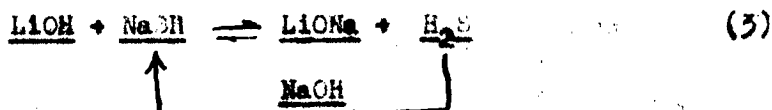
In pure sodium hydroxide the following reaction can occur:



In pure sodium hydrosulfide the analogous reaction is:



In a mixture of sodium hydroxide and sodium hydrosulfide the pulping action is faster than in either one alone. Speculation as to the reason for this might suggest that a reaction may occur according to some such mechanism as shown below, whereby one of the products, hydrogen sulfide, is removed by the sodium hydroxide.



It is apparent from these equations that if only reactions 1 and 2 occur when a mixture of sodium hydroxide and sodium hydrosulfide is used, then the sulfur content of the lignin product will increase directly with the percentage of sodium hydrosulfide in the liquor. But if an additional reaction of the type suggested above (3) can occur, then the sulfur content of the dissolved lignin will be somewhat less than proportional to the sodium hydrosulfide content of the liquor. The results of the above experiment (Figure 3) show that this is not the case. Consequently a reaction of the type of equation 3 is unlikely.

The fact that as many as three sulfur groups (based on the molecular conception of Brauns and Hibbert (23)) can be introduced into the lignin molecule by a reaction with sodium hydrosulfide suggests

that the reaction may consist of a replacement of successive hydroxyl groups by -SH groups:



It is suggested that the major reactions whereby lignin becomes soluble in alkaline solutions are of the type:



and



Since hydrogen sulfide is a stronger acid than water, the hydrogen in the LiSH is more acidic than the hydrogen in the LiOH, and consequently LiSH is more soluble in alkali than LiOH. This affords an explanation for the rapid pulping of kraft liquors. In other words, the theory is proposed that sulfide speeds up the pulping reaction because the sulfur groups introduced into the lignin increase its acid character and make it more readily soluble in alkali.

## E. Further Work with Sodium Hydrosulfide

### 1. Effect of High Concentrations

Studies were made of the effect of varying conditions on the sulfur content of the dissolved lignin. The effect of high concentrations of sodium hydrosulfide was first studied. The procedures were the same as those previously described, except that a small 350-cc. autoclave was used. The results of cooking with very high concentrations of hydrosulfide are presented in Table AII.

TABLE XII

## DIGESTIONS WITH HIGH CONCENTRATIONS OF HYDROSULFIDE

## Cook 75

30 grams wood, 300 cc. liquor  
66 per cent total chemical, 6.6 per cent concentration  
30 minutes to 165° C., 4½ hours at 165° C.

Yield %	Lignin %	Residual Lignin %	Residual Carbo- hydrate %	S in Alkali Lignin %	S in Pulp %	S in Pulp % of Lignin in Pulp
38.55	2.15	0.83	37.72	5.02	0.139	6.47

## Cook 105

25 grams wood, 250 cc. liquor  
102 per cent total chemical, 10.2 per cent concentration  
35 minutes to 165° C., 4½ hours at 165° C.

Yield %	Lignin %	Residual Lignin %	Residual Carbo- hydrate %	S in Alkali Lignin %	S in Pulp %	S in Pulp % of Lignin in Pulp
33.70	1.50	0.50	33.20	5.30	0.278	18.53

The alkali lignin obtained in Cook 75 was a fairly dark red-brown, while that obtained in Cook 105 was a deep blue. In neither case was the sulfur content as high as that obtained previously at lower concentrations. It is noteworthy that the usual light brown alkali lignin products pass rapidly through a red-brown and a deep blue stage under the oxidizing action of the nitric acid used for the sulfur determination. Presumably the high concentration used in the above study resulted in oxidation and degradation of the lignin.

## 2. Effect of Temperature

A study was made of the effect of maximum temperature on the sulfur content of the lignin dissolved by sodium hydrosulfide.



The range 130 - 170° C. was studied. A larger quantity of material was used for the digestions at the lower temperatures. Cooks 130 and 140 were made in the 5-liter autoclave, while Cooks 150 and 170 were made in the 350-cc. autoclave. The results are presented in Table XIII and the data are represented graphically in Figure 4.

TABLE XIII

## EFFECT OF TEMPERATURE ON SULFUR CONTENT OF LIGNIN

Conditions for all cooks:  
40 per cent total chemical, 4 per cent concentration  
65 minutes to temperature, 3 hours at temperature

Cook	Temperature °C.	Yield %	S in Alkali Lignin %
130	130	63.50	4.92
140	140	59.10	6.01
150	150	50.10	3.63
33	160	50.60	10.72
170	170	43.40	6.48

The results show that, under the conditions studied, the amount of sulfur in the alkali lignin increased with increasing temperature to a maximum at 160° C. Above this point it decreased quite rapidly.

In the initial part of the curve the increase appears to be fairly gradual, and the curve may well be asymptotic to some value between 3 and 4 per cent. According to the molecular weight of the lignin unit given by Brauns and Eibert (23), 3.6 per cent sulfur corresponds to one sulfur atom. It is reasonable to suppose that sodium hydrosulfide will not remove lignin without introducing at least one sulfur atom into the lignin molecule.

Between 140 and 160° C. the increase in sulfur content was

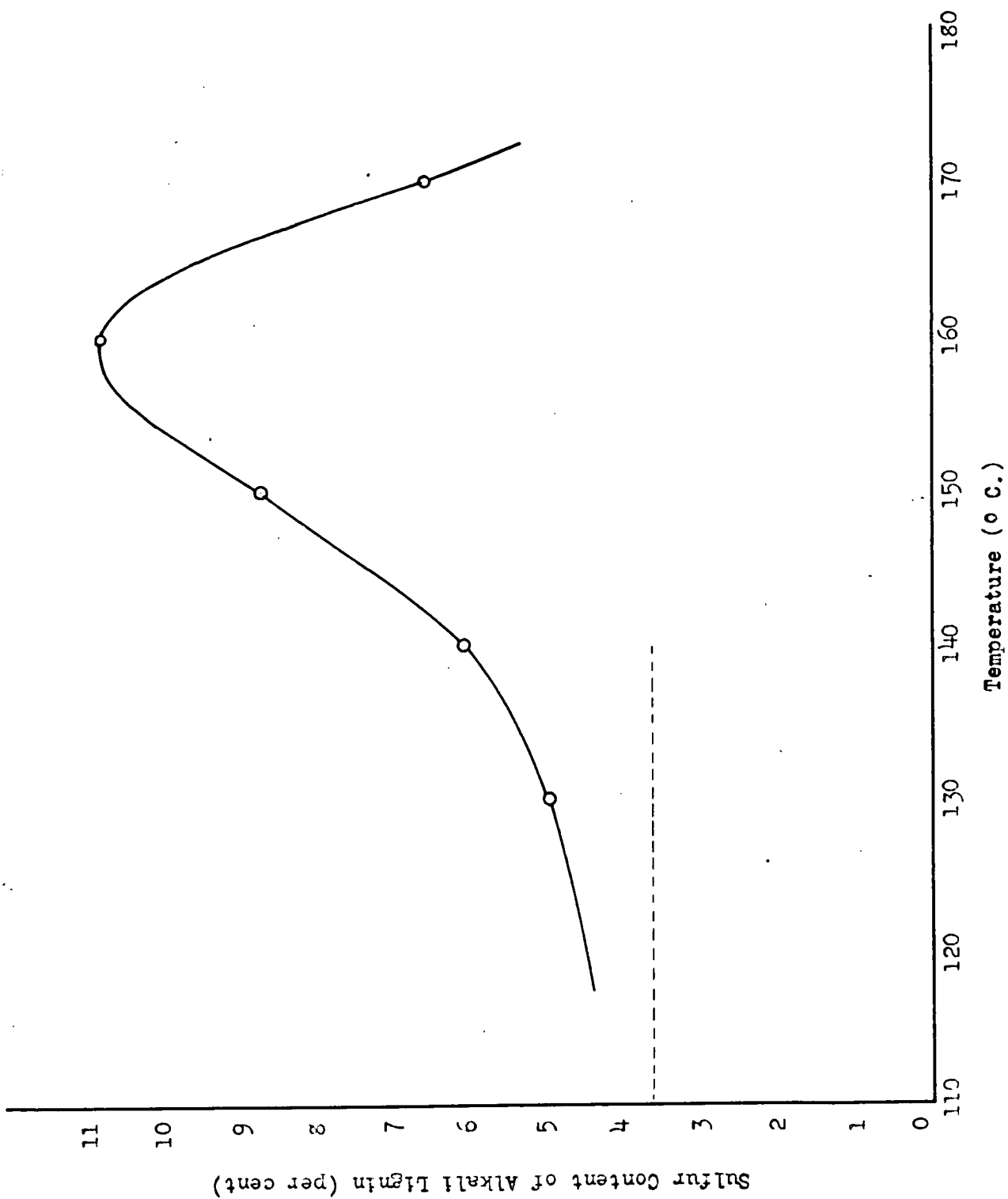


FIGURE 4. The Effect of Temperature on the Sulfur Content of the Lignin Dissolved

essentially linear. On the basis of the molecular weight given by Brauns and Hibbert, the curve indicates that a second sulfur atom was introduced gradually in the range 115 - 145° C. and that a third sulfur atom required greater activity and was introduced to a regularly increasing extent in the range 145 - 160° C. Although nothing has been proved in this dissertation concerning the molecular configuration of these products, it is not an unreasonable guess that the reaction is one of substitution of -SH for -OH in from one to three hydroxyl groups in the lignin.

The lower sulfur content observed above 160° C. may be due either to a decrease in the tendency of the lignin to combine with sulfur or to an increased decomposition of the lignin-sulfur compound under these conditions. In view of the rapid decrease evident here, the latter effect seems more likely and is in accord with the results described in previous sections, which showed that drastic treatment, either at high concentration or for a long cooking time, could result in a product of lower sulfur content than that from a less drastic treatment.

### 3. Reducing Action of Hydrosulfide

It was observed that, in cooks made with sodium hydrosulfide in iron tubes, the pulp and the liquor contained considerable green coloring matter, which changed on standing in the air to a red-brown color.

The action of reducing agents, such as zinc dust plus alkali, will produce a similar green color in kraft pulps. The treatment of a kraft pulp with a warm solution of sodium hydrosulfide is still a better method of producing this green color.

It was found that the material in the liquor which can be reduced to a green color was not in the alkali-lignin fraction, but was

in the fraction insoluble in dioxane. Five grams of alkali lignin from Cook 35 (containing 7.59 per cent sulfur) were digested with 100 cc. of 5 per cent sodium hydrosulfide for 2 hours at  $170^{\circ}$  C. in the 350-cc. stainless steel autoclave. No green coloring matter was found in the liquor. This result indicated that the coloring matter was apparently not a lignin-sulfur compound.

It was found that, when kraft pulps are extracted with oxalic acid, or other acids, no green color is observed on reduction or on treatment with sodium hydrosulfide. It was surmised that the green color is due to iron compounds. Hydrated ferrous sulfide is green, and most ferric compounds are red-brown.

A cook was made in a glass vessel (contained in the 350-cc. steel autoclave, with iron-free chemicals. Thirty per cent total chemical was used at 50 per cent sulfidity. The schedule was 1 hour to  $165^{\circ}$  C. and  $1\frac{1}{2}$  hours at  $165^{\circ}$  C. The pulp did not give a green color with sodium hydrosulfide or with reducing agents, nor did the pulp develop the same deep red-brown color on standing which was observed in the case of the pulps cooked in the iron containers.

The pulps from Cooks 51, 52, 53, and 54 were analyzed for iron, and the results, which are given in Table XIV, show that considerable iron was dissolved. The results did not vary consistently with the compositions of the liquors used, nor did the pulps contain an amount of sulfur equivalent to the amount of iron present. Apparently the iron is not present as ferrous sulfide in the pulp.

TABLE XIV

## IRON CONTENT OF PULPS

Cook	NaOH %	NaSH %	S in Pulp %	Fe in Pulp %
51	75	25	0.187	0.976
52	50	50	0.255	1.113
53	25	75	0.348	0.174
54	0	100	0.385	0.674

Kullgren (15) observed a catalysing effect of iron on digestion of wood with sodium hydrosulfide. He also observed that sodium hydrosulfide liquors are very corrosive. The present work confirms that observation. If a reaction of the following type occurs,



then the catalytic effect can be ascribed to the formation of a small amount of sodium hydroxide, which would speed up the action of sodium hydrosulfide.

The large amounts of iron dissolved in Cooks 51, 52, 53, and 54 may be accounted for largely by the fact that the iron containers used were sections of wrought iron boiler tubing, which is much less resistant to corrosion than steel.

The existence of iron compounds in a reduced condition in the liquor and in the pulps from pure sodium hydrosulfide cooks depends on the fact that sodium hydrosulfide has to some extent a reducing action. The preservation of carbohydrates in a kraft cook cannot well be laid to this reducing action for, as the results of Cooks 73 and 103 show, considerable loss of carbohydrate material can occur if sufficient sodium hydrosulfide is used. Furthermore, the results in Table II show that if sufficient

chemical is present, the destruction of carbohydrate material is about the same at all sulfidities, including zero sulfidity. Probably the favorable preservation of carbohydrates in an ordinary kraft cook is due to the more rapid pulping action which exposes the carbohydrate to a less concentrated liquor for a shorter time. The same considerations apply to the condition of the lignin product obtained from these liquors. The alkali lignin product from a sulfide liquor is much lighter in color than that from a soda liquor. But, as the results of cooks 78 and 108 show, even a sodium hydrosulfide cook may produce a lignin product which is very dark in color if sufficient chemical is used.

#### F. Effect of Sulfur Content of Lignin Residues on Bleachability of Kraft Pulps

A study was made of the effect of the sulfur groups in the residual lignin in a kraft pulp on the bleachability of that pulp.

#### Experimental Procedure

Bleach consumption was determined by the amount of bleaching powder (calculated as 35 per cent available chlorine) required to produce a brightness of 65 as measured on the General Electric reflection meter. Eight-tenths gram samples were used in a volume of 65 cc. in large test tubes. The temperature employed was 55° C. The test sheets were made on the British standard sheet mold. The brightness readings of a series of trial bleachings were plotted against the percentage of bleach used, and the value at 65 brightness was taken.

It was found necessary to defiber the pulps thoroughly with a malted-milk stirrer in order to obtain consistent results. Pulps which were not cooked uniformly were not comparable with uniform pulps, i.e., the results were higher. For this reason several of the pulps, which had been previously prepared, could not be used. It was also found necessary to extract iron from the pulps before bleaching in order to obtain consistent results. This was accomplished by treating each pulp with 2 per cent sulfuric acid at 1 per cent consistency for three minutes at room temperature and then washing thoroughly with cold water.

Several pulps of known sulfur and lignin contents had already been prepared in previous experiments. These pulps gave the following results.

TABLE XV  
BLEACHING STUDIES

Cook	Lignin %	S in Lignin %	Bleach Consumption %
32	12.60	1.64	77.5
51	6.93	2.70	50.8
52	7.13	3.60	58.6
53	9.39	3.60	75.2
108	1.50	18.50	4.0
33	5.77	3.08	45.3
75	2.15	6.47	8.9
44	1.85	12.70	13.3
65BR	4.97	3.00	38.7

Six additional pulps were prepared with soda liquors, and with kraft liquors in the commercial range of sulfidities. The results follow:

TABLE XVI  
FURTHER BLEACHING STUDIES

Cook	Lignin %	S in Lignin %	Bleach Consumption %
S-1	2.76	0	15.3
S-2	7.26	0	40.0
K-1	7.21	1.14	47.0
K-2	9.56	0.94	53.0
K-3	8.71	0.98	52.0
K-4	5.00	1.43	35.0

All of the above data are plotted in Figure 5.

These results show a regular increase in bleach requirement with an increase in the sulfur content of the residual lignin in a

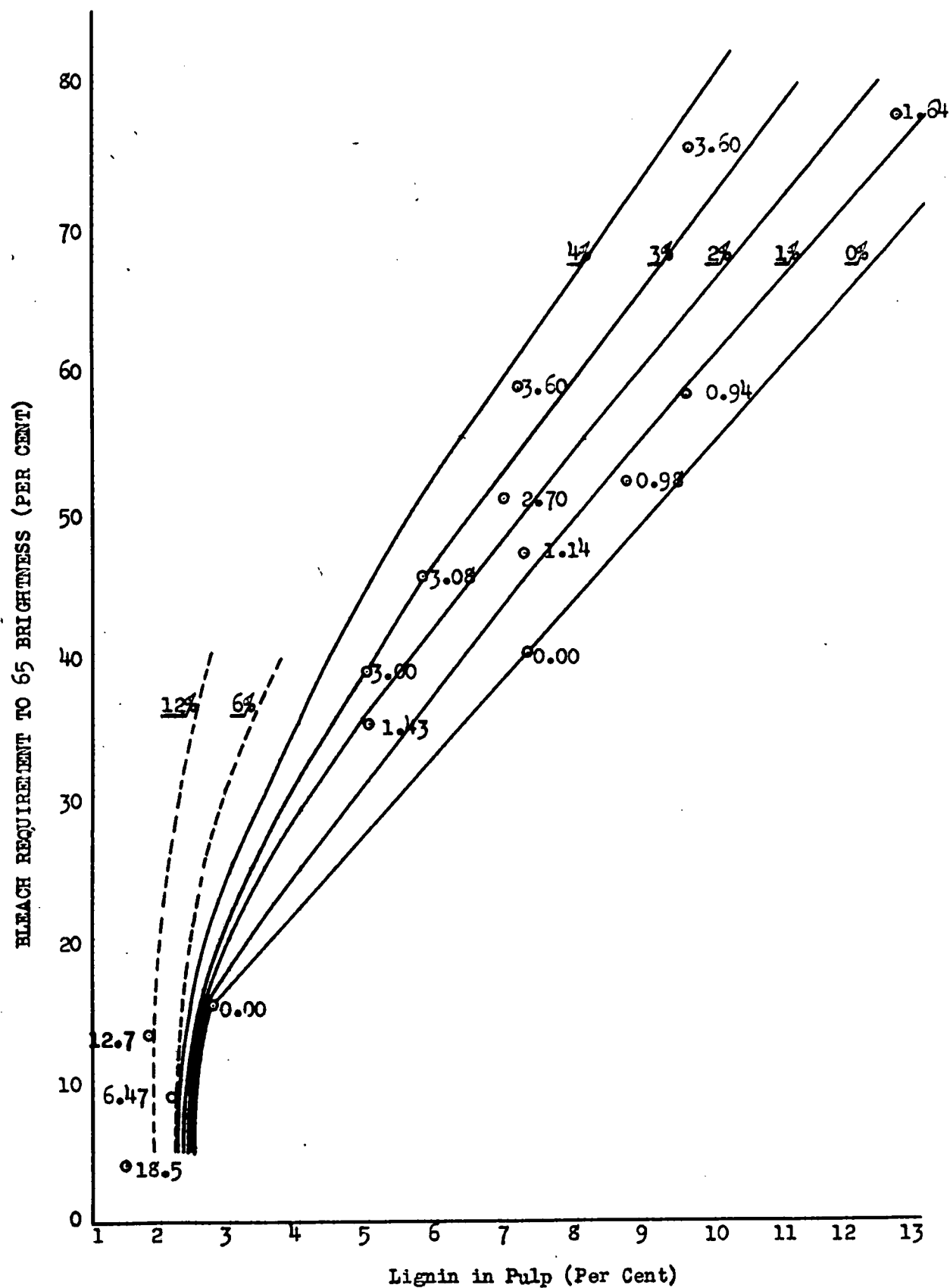


FIGURE 5. THE EFFECT OF THE SULFUR CONTENT OF THE LIGNIN RESIDUES ON THE BLEACH REQUIREMENT OF ALKALINE PULPS.



kraft pulp. It is indicated that the sulfur content of the lignin is a factor of relatively minor importance in the problem of bleaching kraft pulps. Pulps in the commercial range all contain approximately 1 per cent sulfur in the lignin.

An answer to the question of the relative difficulty in bleaching softwood soda and kraft pulps is given in Figure 5. It would appear that the difficulty in bleaching kraft (and soda) pulps is due to the nature of the alkaline-treated lignin residue in the pulps. Sulfite pulps bleach much more easily than alkaline pulps because the sulfonated lignin residue requires little action to make it soluble in an alkaline calcium hypochlorite solution.

There is no apparent evidence in Figure 5 in support of the "sulfur dyestuff" theory which presupposes the existence of small amounts of a sulfur dyestuff in kraft pulps. Evidence contrary to this theory is afforded by the linear relationship between lignin content and bleach consumption, which indicates that the lignin is the important item. In Cook 103, which was cooked to 1.5 per cent lignin, the pulp required only 4 per cent of bleaching powder to reach 65 brightness (only 10 per cent to reach 74 brightness, and only 15 per cent to reach 80 brightness -- a linear relationship). Apparently, then, from these results, the difficulty in bleaching kraft pulps cannot be ascribed to a dyestuff which is taken up from the liquor, but to the lignin residues themselves.

In the above tables the sulfur contents of the lignin residues in the extremely well cooked pulps are probably too high. At the low lignin contents in question, a very small amount of sulfur present in any other manner becomes important enough to give fictitiously high values

for the sulfur content of the lignin.

The deviation of the curves in Figure 5 from the linear relationship at low lignin contents means that, as the lignin content becomes very low, the unbleached pulp approaches 65 brightness.

### G. Effect of Preliminary Impregnation with Hydrosulfide

It was thought that preliminary impregnation of chips with the sodium hydrosulfide component of a kraft liquor, followed by a cook with the sodium hydroxide component, might produce more rapid pulping than the ordinary method. With the sodium hydrosulfide initially present within the chips, it was thought that the higher sodium hydrosulfide concentration thus obtained might produce a more rapid combination of the sulfur with the lignin, and that the sulfur-lignin compound might afterwards dissolve quite readily in the sodium hydroxide — making the whole process more rapid.

### Experimental Procedure

Six hundred grams of southern pine chips were impregnated for 20 minutes at 100-lb. nitrogen pressure at 60° C. with 3000 cc. of 3 per cent sodium hydrosulfide in the 5-liter autoclave. The chips absorbed 690 cc. of liquor. The remaining 2310 cc. was found by titration to contain 2.46 per cent sodium hydrosulfide — a very definite reduction. The chips had absorbed 33.2 grams of sodium hydrosulfide, or 3.53 per cent of the weight of the wood. If 27.5 per cent of total chemical is used, 3.53 per cent sodium hydrosulfide corresponds to a sulfidity of 40.2 per cent. Enough sodium hydroxide was added to make 27.5 per cent total chemical, and water was added to bring the total concentration to 4 per cent. The contents of the digester were raised in 1 hour to 170° C. and held at this temperature for 1 hour, 15 minutes. The pulp obtained was compared with a pulp cooked in the ordinary way with a 40.2 per cent sulfidity liquor at 27.5 per cent total chemical and 4 per cent concentration, and according to the same temperature schedule.

The data for the above cooks are presented in Table XVII.

TABLE XVII

## EFFECT OF PRELIMINARY IMPREGNATION WITH HYDROSULFIDE

	Screenings %	Screened Yield %	Lignin in Pulp %	Residual Lignin %	Residual Carbohy- drate %
NASH-impregnation	5.00	44.40	8.88	3.94	40.46
Ordinary cook	5.33	43.00	6.03	2.59	40.41

The results show that preliminary impregnation with the sodium hydrosulfide component of a kraft liquor did not accelerate the pulping rate, but, on the contrary, decreased it somewhat. Apparently sodium hydrosulfide reacts with wood rather slowly when present alone, and the more rapid pulping action does not take place until both components of the liquor are dispersed throughout the chip. The entrance of the sodium hydroxide in the case of the impregnation cook was necessarily by diffusion, which is a slower process than the usual penetration.

#### H. Recent Work at the Forest Products Laboratory

While the present work was in progress a paper on the "Sulphidity Effect in the Sulphate Pulping of Douglas Fir" was presented at the annual meeting of the Technical Association of the Pulp and Paper Industry by Bray, Martin, and Schwartz (24) of the Forest Products Laboratory.

These investigators assumed that the activity of sodium sulfide is equal only to the amount of sodium hydroxide formed through its hydrolysis. In other words, they proposed to calculate the active chemical in a kraft liquor on the basis of the total sodium hydroxide (the

free sodium hydroxide plus essentially one half of the sodium sulfide). On this basis, as the sulfidity of a liquor is increased, the actual total chemical would have to be increased regularly to maintain the same concentration of active chemical.

Bray, Martin, and Schwartz made a series of digestions of Douglas fir wood for which the calculation of chemical was made in the above manner. The range 0 - 100 per cent sulfidity was studied. The actual total chemical was 20 per cent at 0 sulfidity and was increased regularly to 39 per cent at 100 per cent sulfidity to maintain the sodium hydroxide component at 20 per cent. It was found that the degree of delignification increased progressively up to a sulfidity of 34 per cent. In the range 34 to 100 per cent sulfidity the degree of delignification was essentially constant.

It has been shown in this dissertation that the assumption on which Bray, Martin, and Schwartz based their calculation is incorrect from a theoretical point of view. Actually, no claim for theoretical accuracy on this point was made in their paper.

In the liquors used in their investigation the amount of the sodium hydroxide component of the kraft liquor was constant at 20 per cent, and the sodium hydrosulfide component progressively increased as the sulfidity was increased. An increase in rate of delignification was naturally observed with an increase in the amount of sodium hydrosulfide up to the maximum amount of sodium hydrosulfide with which the lignin could combine. A further increase in the amount of sodium hydrosulfide produced no effect.

## III. COMPREHENSIVE SUMMARY

On the basis of the experimental investigations described in the preceding pages, the following conception of the action of sulfide in the kraft pulping process is proposed.

The addition of sodium sulfide to a soda cooking liquor increases the rate of its delignifying action and results in a stronger pulp. The sodium sulfide is essentially completely hydrolyzed at cooking temperatures into sodium hydroxide and sodium hydrosulfide. Either sodium hydroxide or sodium hydrosulfide alone will pulp wood, but rather slowly. When both compounds are present in the liquor the delignifying action is faster. The reason for this is that the reaction of sodium hydrosulfide with the lignin forms lignin-sulfur compounds which dissolve quite rapidly in sodium hydroxide.

The fact that as many as three sulfur atoms (based on the molecular conception of Brauns and Hibbert) can be introduced into lignin by a reaction with sodium hydrosulfide, suggests that the reaction may consist of a replacement of successive hydroxyl groups by -SH groups:



On the basis of the present work, it is suggested that the major reactions whereby lignin becomes soluble in alkaline solutions are of the type:



and



Since hydrogen sulfide is a stronger acid than water, the hydrogen in the LiSH is more acidic than the hydrogen in the LiOH, and consequently LiSH is more soluble in alkali than LiOH. This affords a mechanism for the more rapid solution of the lignin-sulfur compound in sodium hydroxide.

The increase in the pulping rate of a kraft liquor increases with the amount of sulfide only up to a certain point; beyond this optimum sulfidity the replacement of sodium hydroxide by sodium sulfide results in a decrease in delignifying power. The reason for this is that while only about 20 per cent of sodium hydroxide is required to completely pulp wood, twice this amount of sodium hydrosulfide is required to accomplish the same result. Consequently, as the sulfidity of a liquor is increased at constant total chemical, the effectual total chemical is decreased. It also follows from this reasoning that, in the ordinary limited range of total chemical, it is not possible to pulp above certain sulfidities. In other words, a definite minimum of sodium hydroxide is necessary in the cooking liquor with limited total chemical. Furthermore, the minimum amount of chemical required to pulp wood at a given sulfidity increases regularly with the sulfidity. As a still further consequence of these facts, the value of the optimum sulfidity increases regularly with an increase in total chemical. For, as the total chemical is increased, the point where the minimum amount of necessary chemical is approached occurs at higher sulfidities.

The value of the optimum sulfidity is not affected by changing concentration in the range 0 - 6 per cent concentration. This is good evidence that sodium sulfide is essentially completely hydrolyzed at cooking temperatures. For, if the hydrolysis were incomplete, the change in the degree of hydrolysis with a change in concentration would result in a shift in the optimum sulfidity.

Very recent work at the Forest Products Laboratory indicates that if the total sodium hydroxide in kraft liquors is held constant, by increasing the total chemical as the sulfidity is increased, then increased delignification is observed up to  $\frac{3}{4}$  per cent sulfidity, and above this

sulfidity there is no further change. The explanation for this result is that if the sodium hydroxide component is held constant while the sodium hydrosulfide component is increased, the rate of delignification will increase up to the point where the lignin can combine with no more sodium hydrosulfide. An increase in the amount of sodium hydrosulfide beyond this point has no effect.

The existence of iron compounds in a reduced condition in the liquor and in the pulps from pure sodium hydrosulfide cooks depends on the fact that sodium hydrosulfide has to some extent a reducing action. The experimental evidence obtained in this work indicates that this reducing action is not primarily responsible for the protection of carbohydrates in a kraft cook. It appears likely that the superior preservation of carbohydrates and of the strength of the pulp, which occurs in kraft cooking, is very largely dependent on the rapid delignifying action. This rapid action results in the exposure of the carbohydrate material to the action of a weaker liquor for a shorter time than is the case in soda pulping.

The sulfur groups in the lignin residues in a kraft pulp make the pulp slightly more difficult to bleach. But this is not an important factor. Soda pulps are very nearly as difficult to bleach as kraft pulps. It appears that the difficulty in bleaching kraft and soda pulps is due to the alkaline-treated lignin residue in the pulps. No experimental evidence was obtained to indicate the existence of a sulfur dyestuff in kraft pulps.

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