

AN ABSTRACT OF THE THESIS OF

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for the M.S. in Chemistry

(Name)

(Degree)

(Major)

Date Thesis presented May 5, 1938

Title The Fractionation of Waste Sulfite Liquor.

Redacted for Privacy

Abstract Approved:

(Major Professor)

The nature of waste sulfite liquor is discussed with special emphasis upon its effect in stream pollution and upon its potential economic value. In order to scientifically attack the problem of producing a suitable by-product from the liquor, the nature of the lignin sulfonic acids which make up the principle solid constituent must be better understood.

Fractionation of the liquor has been accomplished by the use of aromatic amines and lead acetate. This work has previously been done on liquor from Eastern and European woods. Hagglund (5) and Tomlinson and Hibbert (16) report that they were unable to remove a portion of the lignin sulfonic acids upon the addition of quinoline HCl, and a subsequent fraction upon the addition of beta-naphthylamine HCl. Freudenberg and co-workers (3) were unable to obtain any fraction other than that precipitated with quinoline.

In this work a commercial waste sulfite liquor prepared from western hemlock wood was used. Three fractions were obtained in yields of 73.0, 15.4 and 11.6% from quinoline, beta-naphthylamine and lead acetate, respectively. This corresponds to yields of 70, 16 and 14% obtained by Tomlinson and Hibbert (16).

The fractions were purified, and complete elementary analyses were made on the first two fractions. All three were analysed for methoxyl content. Results throughout are comparable to those obtained in a previous investigation (16). It is believed that waste sulfite liquor is in general composed of at least three distinct lignin sulfonic acids.

FRACTIONATION OF WASTE
SULFITE LIQUOR

by

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A THESIS

submitted to the
OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1938

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FRACTIONATION OF WASTE SULFITE LIQUOR

I. INTRODUCTION

In the manufacture of sulfite pulp, the essential feature of the process is the removal of the lignin from the wood. This results in the formation of water soluble lignin sulfonic acids, the latter existing as their calcium salts in the so-called waste sulfite liquor.

Walker (17) describes the waste liquor as a dark, reddish-brown fluid of a specific gravity of about 1.05 and having a peculiar, not unpleasant odor. Among the constituents present he mentions sulphur dioxide, sulphur trioxide, free sulphur, calcium lignin sulphonates, pentoses and pentosans, mannose, dextrose, galactose, free furfural, traces of vanillin and small quantities of terpene-like substances.

For every ton of dry fiber produced the waste liquor contains approximately one ton of dissolved organic materials. Of this amount, 1300 pounds are lignin and 700 pounds are carbohydrates; proteins, rosin and fat occur in only relatively small amounts.

The problem presented by the waste liquors of the sulphite process is one which is not only interesting from a chemical standpoint but has also attracted much

attention because of its bearing on stream pollution. In some cases, particularly in Europe, mills have been obliged to close because it has been found impossible to purify the waste liquors sufficiently to comply with the legal requirements. While the industry in the United States is not confronted with quite such serious conditions it is only a question of time before much more purification will be demanded. The discharge of such vast quantities of waste into streams renders the water injurious to health, makes it unfit for boiler use, aids in the development of algae, and under certain conditions it may cause the development of hydrogen sulfide with accompanying loss of oxygen in the water and consequent death of animal and vegetable life (15).

In addition, waste of such enormous magnitude has led many investigators to take hold of the problem with the desire to obtain a by-product which will at least pay for disposal of the liquor.

Attempts to utilize the materials in the waste liquor have been very numerous and many patents have been issued covering all kinds of industries. Mention of some of these uses is all that will be given here.

As a binder, it has been used on roads and in the manufacture of briquettes; as fertilizer, as an aid in tanning, as a source of ethyl alcohol and as a fuel it

has been of moderate application.

While much progress has been made there is still a tremendous amount of work to be done. Lignin, which may be defined loosely as the non-cellulose portion of the wood (excluding rosin, sugars, etc.), must be looked to as the source of some profit-producing substance. Before this can be accomplished, the chemistry of lignin must be better understood.

The first studies on lignin led to the belief that it was a single substance. The present viewpoint is well expressed by Kürschner (11) who believes that lignin is probably a mixture of closely related compounds. He states further that so far no one has prepared pure lignin with certainty. Lignin (12) as isolated by ordinary chemical processes or by means of a fungus is not like the natural compound in the tree. For instance, as a result of acid treatment, lignin may polymerize, resinify, condense or carbonize and become somewhat changed as a result of the loss of water.

A conclusion made by Kürschner (11) is that methods based on the recovery of lignin from sulfite solutions obtained in pulp-making are worthless, because the lignin so brought into solution has suffered far-reaching decomposition. This, it is believed, does not lessen the value of studies made on the lignin sulfonic acids. Characteristics of the acids must be derived from the

lignin and introduction of an SO_3H group does not impose serious difficulties in their study. In addition, most of the interest in lignin exists because of the desire and necessity of utilizing waste sulfite liquor.

Since waste sulfite liquor can be fractionated, it is generally conceded that it contains at least two distinct sulfonic acids. Klason (9), (10) and Hägglund (5) have found that a portion of the lignin sulfonates can be salted out by calcium or sodium chloride. The remaining portion is precipitated as the lead salt of the lignin sulfonic acid upon the addition of basic lead acetate. Tomlinson and Hibbert (16) further separated the calcium chloride precipitate into two fractions, the one most readily salted out, and the one least readily.

Another more satisfactory method is the precipitation of a fraction, generally termed alpha-lignin sulfonic acid, by the addition of aromatic amines. The remaining portion, beta-lignin sulfonic acid, is precipitated from the filtrate as the lead salt by the addition of basic lead acetate.

Klason (9), (10) has stated that the alpha-fraction consists of 67% of the total lignin content of the wood and the beta-fraction about 30%. He considered the former to be identical with the Ca-lignosulfonate salted out by sodium or calcium chloride. The two fractions, he concluded, are essentially very similar, fractionation

being possible by the presence in the alpha-lignin of an acrolein group in contrast with an acrylic acid group in the beta-lignin.

Hägglund (5) has taken exception to the work of Klason and presented experimental evidence to the contrary. Addition of an aromatic amine causes the precipitation of a considerably larger quantity of alpha-fraction than does calcium chloride. The yield was also shown to be dependent on the nature of the amine used.

The observations of Hägglund have been confirmed by Tomlinson and Hibbert (16). They found that the degree of efficiency of the various reagents as precipitants increased in the following order: sodium chloride, calcium chloride, quinoline and iso-amylamine, beta-naphthylamine and finally lead acetate. They conclude that the old nomenclature of alpha- and beta-lignin is entirely inadequate for such a complex mixture, but give no explanation for the difference in the precipitating ability of the different amines.

Hägglund (6) states that the assumption has been made that the alpha- and beta- fractions represent chemical individuals, components of native lignin. Experimental evidence is given to show that beta-lignin does not exist as such in spruce wood but is a degradation product of lower molecular weight, formed by heating with acid sulfite solutions. The relative amounts of alpha- and

beta-lignin depend primarily upon the pulping conditions used. An oxidation-reduction system is formed with the bisulfite sugars and lignosulfonates, yielding finally gluconic acids and lignin sulfonic acids not precipitable with aromatic amines.

Freudenberg and co-workers (3) have reported that they were unable to obtain any fraction other than that precipitated by quinoline, a result contrary to that found by Hägglund (5) and Tomlinson and Hibbert (16).

That the chemical composition of the various fractions differs has been pointed out by Hägglund (5). He found differences in the methoxyl and sulfur content of two beta-fractions prepared from the same liquor, one having been obtained after removal of the alpha-fraction with quinoline, the other after removal of the alpha-fraction with alpha-naphthylamine. No analyses are given for the two alpha-fractions, but it would seem reasonable that their composition changed correspondingly.

Tomlinson and Hibbert (16) have analyzed alpha-fractions obtained from quinoline, from beta-naphthylamine, and from beta-naphthylamine after previous removal of the quinoline fraction, and the corresponding beta-fractions for methoxyl, sulfur and potassium. Differences found are quite similar to those to be reported in this paper.

STATEMENT OF PROBLEM

This work was undertaken in an attempt to obtain a more extended knowledge of the lignin sulfonic acids produced in the sulfite pulping process. Previous to this time, the method of fractionation outlined in the following pages has been tried only on waste liquor obtained from Eastern and European woods. The same general procedure employed by Freudenberg (3) and later by Tomlinson and Hibbert (16) was followed in order to get a comparison of the yields of the various fractions obtainable from a western hemlock waste liquor. Analyses of these fractions were made to point out any dissimilarities existing between them and also to show the similarity of the lignin sulfonic acids obtained from different sources.

EXPERIMENTAL

Source of Calcium Lignin Sulfonates

Commercial waste sulfite liquor was obtained from Rayonier Inc., Shelton, Washington. It was produced from a regular cooking schedule, using calcium bisulfite cooking liquor. Previously untreated western hemlock wood was cooked, the resulting liquor having a density

of 1.047 and containing 11.1% total solids and 1.03% ash, based on the weight of the waste liquor.

Preparation of Fraction K L.S.A. I.

One-half liter of dilute liquor was dialysed for three days in a cellophane sack against running tap water. The very dilute solution was then concentrated under vacuum to 400 ml., filtered, and 100 ml. of 10% quinoline hydrochloride solution added slowly with constant stirring. A light chocolate-colored precipitate formed, from which the supernatant liquid was decanted. The precipitate was dissolved by adding 1 N. potassium hydroxide until solution was complete. The dark brown solution obtained was at first cloudy due to the presence of the quinoline which was precipitated by the base. This solution was again made slightly acid with HCl, water added to bring the volume to 400 ml., and quinoline hydrochloride solution added, as before, until the precipitate, upon standing a few minutes, settled out as a black, gummy mass. This procedure of adding an excess of the amine hastens the time required for the precipitation and re-resolution considerably. The voluminous precipitate first formed must otherwise be centrifuged in order to obtain a good separation of the liquor. The procedure results in complete reprecipitation of the lignin sulfonate. It was carried out five times in all.

The combined mother liquors from the five pre-

precipitations were made slightly alkaline, concentrated under reduced pressure, dialysed for 24 hours to remove the excessive amount of salt present, and again concentrated to a volume of 200 ml. Quinoline hydrochloride was added in excess and the precipitation carried out five times as before.

Each solution was made alkaline, extracted with ether to remove the quinoline, and dialysed for seven days. The ligninsulfonic acid was recovered by evaporating the solutions to dryness under reduced pressure at 70°C. The main alpha-fraction amounted to 14.2 grams and the second, 1.5 grams; total yield 15.7 grams.

The material was further purified by dissolving the combined yields in the least possible amount of water and precipitating it by slow addition of absolute dioxane (20 volumes) accompanied by vigorous stirring. The product was centrifuged off and dried as before.

Preparation of Fraction K L.S.A. II.

The mother liquors from the quinoline precipitations were combined, made slightly alkaline, concentrated to 200 ml., and extracted with ether. A saturated solution of beta-naphthylamine was added in excess yielding a precipitate much like that obtained previously. The precipitate was dissolved in 1 N. potassium hydroxide, diluted to 200 ml., made acid, and this procedure was

repeated four times in all. The potassium lignin sulfonate was regenerated, extracted with ether, dialysed and precipitated in the same manner as the K L.S.A. I; yield 3.3 grams.

Preparation of Fraction K L.S.A. III.

The combined mother liquors from the beta-naphthylamine precipitations were made slightly alkaline and extracted with ether. The solution (about 1.5 liters) was made neutral to litmus, and a 10% solution of basic lead acetate was added slowly with stirring. The precipitate was centrifuged off, and washed four times by suspending it in one-half liter of distilled water. The ligninsulfonic acid was regenerated from its lead salt by gradual addition of one percent acetic acid and the lead precipitated by addition of 5% sulfuric acid. After centrifuging off the lead sulfate, the solution was made basic and dialysed for three days. The solid was then reprecipitated by dioxane as before; yield 2.5 grams.

Determination of Methoxyl Groups

The procedure adopted was that modified by Clark (1). The apparatus constructed differed slightly in detail of construction but operated essentially the same as the apparatus described in the preceding reference.

Approximately 20 mg. of substance upon a balanced

piece of cigarette paper were weighed on an ordinary analytical balance sensitive to 0.1 mg. About 2.5 ml. of phenol and 5 ml. of constant boiling hydroiodic acid solution were added to the boiling flask together with the sample and a little porous tile to prevent bumping. Red phosphorous, purified by washing in water, ether, alcohol and much water, and cadmium sulfate were used in the trap to purify the gas stream. The contents of the absorption tubes were washed into 150 ml. beakers with addition of 75 ml. of water, made acidic with nitric acid, and heated on a steam bath overnight. The precipitate of silver iodide was weighed in tared gooch crucibles.

Results of analyses are to be found in Table I.

Determination of Carbon and Hydrogen Content

This procedure was carried out as directed by Fisher (2). The combustion train consisted of pre-heater, Dehydrite- and ascarite-filled bottles for purifying the oxygen, and a three-unit, electrically heated combustion furnace. Water vapor was collected in an absorption bottle filled with Dehydrite; carbon dioxide was adsorbed in a similar bottle containing ascarite. The absorption bottles were weighed against a tare.

Table I
Methoxyl Group Analyses

K L.S.A. Fraction I.

Run	%OCH ₃	%OCH ₃ based on "Lignin"
1	12.88	
2	13.59	
3	11.92	
4	13.33	
5	11.85	
6	12.49	
Average	12.67	16.12

K L.S.A. Fraction II.

1	9.62	
2	9.70	
3	9.80	
4	9.73	
Average	9.71	13.16

K L.S.A. Fraction III

1	9.58	
2	9.13	
3	9.01	
4	9.52	
Average	9.31	..

Blank runs were made until the bottles came to constant weight. The apparatus and procedure were tested on pure sucrose. Results of the analyses are to be found in Table II.

Determination of Sulfur Content

This procedure followed the technique devised by Parr (13), using the standard Parr-Burgess sulfur bomb. Two grams of potassium chlorate, twice the amount of accelerator recommended for a half gram sample of coal, were used in order to get complete oxidation of the potassium lignin sulfonate. No preliminary runs were made, the procedure being considered reliable.

Determination of Potassium

This was done according to the procedure of Partansky and Benson (14). After being finely ground, one half gram samples were burned in a weighed silica crucible. The ash was moistened with 0.3 ml. of concentrated sulfuric acid and an equal volume of water, then dried very slowly over a burner to avoid spattering. The crucible and contents were heated at cherry red heat over a Fisher burner to constant weight and the potassium calculated from the weight of potassium sulfate.

Table II

Carbon and Hydrogen Analyses

K L.S.A. Fraction I.

Run	% H ₂	% C	% H ₂ based on "Lignin"	% C based on "Lignin"	% O ₂ based on "Lignin"
1	4.88	52.89			
2	4.80	52.71			
3	4.67	52.73			
4	4.64	52.63			
Ave	4.75	52.74	6.04	67.12	26.84

K L.S.A. Fraction II.

1	4.56	48.45			
2	4.53	47.91			
3	4.51	48.05			
Ave	4.53	48.13	6.14	65.22	28.64

Sucrose

1	6.57	41.49			
2	6.59	42.08			
3	6.67	41.91			
Ave	6.61	41.82			
Theoret- ical	6.46	42.09			

Table III
Sulfur Analyses
K L.S.A. Fraction I.

Run	% S	% SO ₃ H	% "Lignin"* on SO ₃ H and K-free basis
1	6.53		
2	6.15		
3	6.43		
4	6.18		
Average	6.32	15.99	78.58

K L.S.A. Fraction II

1	7.41		
2	7.29		
Average	7.35	18.60	73.80

* % "Lignin" = 100% - (% SO₃H + % K)

Potassium Analyses

K L.S.A. Fraction I

Run	% K
1	5.43
2	5.42
Average	5.43

K L.S.A. Fraction II

1	7.59
2	7.61
Average	7.60

IV. DISCUSSION

The calcium lignin sulfonates from the liquor were separated into the fraction precipitated with quinoline designated K L.S.A. I, and those remaining were separated into fractions K L.S.A. II and K L.S.A. III, the former representing that precipitated on addition of beta-naphthylamine and the latter, that recovered by lead acetate. During the purification processes the calcium salts were entirely converted to the potassium salts by dissolving the precipitates in potassium hydroxide. This, rather than calcium hydroxide, was used because of its

greater solubility. The symbol K L.S.A. I refers to the potassium salt of ligninsulfonic acid fraction I. The fractionation scheme is outlined in Diagram I.

The yields of the three fractions were 73.0, 15.4 and 11.6% respectively. This corresponds to yields of 70, 16 and 14% obtained by Tomlinson and Hibbert (16) from spruce lignin sulfonic acids. It is not yet known whether this slight difference in behavior is due to the nature of the wood, the difference in cooking schedule, or both.

Based on an approximate theoretical amount of lignin present in the liquor, only 50-60% was recovered. The loss probably occurred during dialysis. A similar behavior has been reported previously by Fuchs (4), Hennig (8) and Tomlinson and Hibbert (16).

It has been found that the sulfur content of a ligninsulfonic acid depends on the time and temperature of the sulfite cook (7). A product having a high sulfur content is obtained on prolonged heating, making it unlikely that any stoichiometric relationship exists between sulfur and lignin (16). The ratio of sulfur in fractions I-A and II-A (Table V) agrees quite closely to the ratio of sulfur in fractions I-B and II-B, although the actual values differ somewhat as may be expected.

Table V

Summary of Analyses of the Potassium
Lignin Sulfonates

%	K L.S.A. Fractions					
	I		II		III	
	A*	B*	A	B	A	B
S	6.3	5.4	7.4	6.6	..	5.6
SO ₃ H	16.0	13.7	18.6	16.7	..	14.2
K	5.4	3.7	7.6	5.0	..	5.8
"Lignin" on K and SO ₃ H free basis	78.6	82.6	73.8	78.3	..	80.0
OCH ₃	12.7	12.8	9.7	12.0	9.3	9.2
OCH ₃ based on "Lignin"	16.1	15.5	13.1	15.3	..	11.5
C based on "Lignin"	67.12	..	65.22
H ₂ based on "Lignin"	6.04	..	6.14
O ₂ based on "Lignin"	26.84	..	28.64

A* Results obtained in this investigation.

B* Comparable results obtained by Tomlinson
and Hibbert (16).

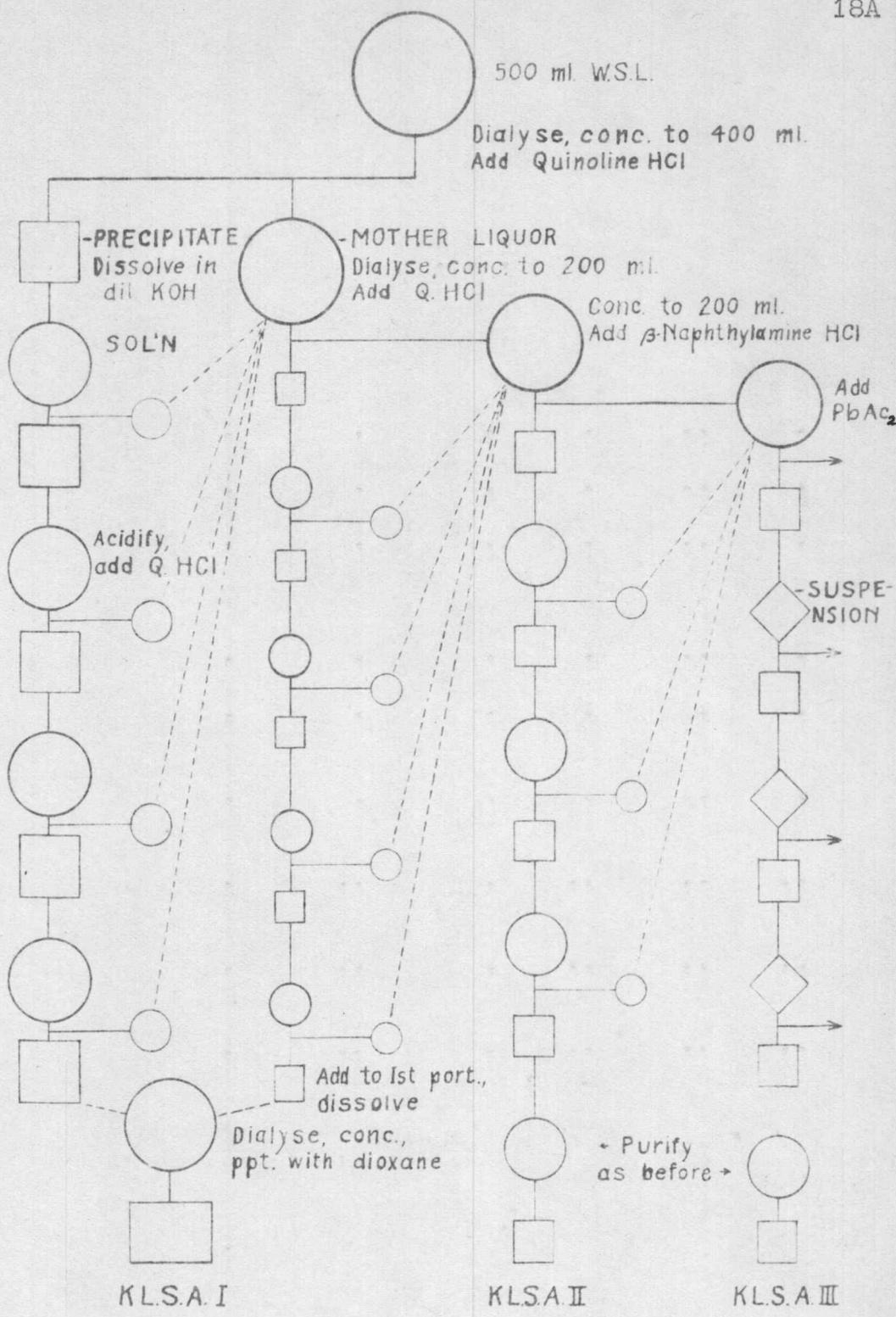


DIAGRAM I. FRACTIONATION SCHEME

The atomic ratio of potassium to sulfur is less than one in all cases. This loss of potassium ions is a result of hydrolisis during the dialysis (16). Determination of potassium was necessary to calculate the amount of "Lignin."

The methoxyl content of the various fractions, based on "Lignin", show little agreement, while Tomlinson and Hibbert (16) found a moderate agreement in the case of those fractions capable of being precipitated with amines.

Although it might be expected that the ratio of carbon to oxygen would be lower in fraction I, due to its higher methoxyl content, the reverse was found true. While the difference is not great, it is outside the range of experimental error. Elementary analysis is not enough to show any fundamental differences in the various fractions, but indicates the presence of different groups as constituents of the lignin sulfonic acid fractions.

No analyses except methoxyl were made on K L.S.A. III. It is considered from the results of the analyses, that very good agreement is shown in the characteristics of the western hemlock lignin sulfonic acids as compared to those of the spruce lignin sulfonic acids (16). The properties of waste sulfite liquors from Western hemlock

wood agree very well with the properties of spruce waste liquor which have been described by Hägglund (5) and Tomlinson and Hibbert (16) but not with those of Freudenberg and co-workers (3). In general, waste sulfite liquor may be considered to contain, at least three distinct lignin sulfonic acids, although they are not found in the same proportions in all waste liquors. This is to be expected since very arbitrary methods were used in the preparation of the waste liquors.

V. SUMMARY

The nature of waste sulfite liquor and its economic importance are discussed. Previous work on the fractionation of ligninsulfonic acids is discussed, particularly the method which makes use of aromatic amines. This same method has been used in the laboratory to secure three fractions designated K L.S.A. I, K L.S.A. II and K L.S.A. III. The potassium lignin sulfonic acids were obtained in yields of 73.0, 15.4 and 11.6% respectively. These correspond to yields of 70, 16 and 14% obtained by Tomlinson and Hibbert (16). The proportion of fractions I and II was almost exactly the same in each case, the lower yield of fraction III in this work changing the relative percentage somewhat. Complete elementary analyses were run on all fractions

with the exception of fraction III.

The results obtained are in good agreement with those of Hägglund (5) and Tomlinson and Hibbert (16) but not with those of Freudenberg and co-workers (3).

VI. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Leo Friedman who suggested this work and offered many helpful suggestions. Also to Rayonier, Inc., for supplying waste sulfite liquor, and to Dr. Charles S. Pease and to Dr. J. W. Ferguson for valuable assistance, the author expresses his indebtedness.

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