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**A Fundamental Study of the Reaction  
Between Kraft Black Liquor and Nitrobenzene**

by William R. Csellak

June, 1950

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**A FUNDAMENTAL STUDY OF THE REACTION  
BETWEEN KRAFT BLACK LIQUOR AND NITROBENZENE**

A thesis submitted by

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in partial fulfillment of the requirements  
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## INTRODUCTION

Approximately 55 pounds of material are lost or burned per 100 pounds of moisture-free wood in preparing 45 pounds of unbleached kraft pulp. Of these losses, approximately 50% are lignin. The aromatic nature of lignin indicates the possibility of preparing from it a host of organic compounds with many times the value of its present use as a fuel.

Numerous investigations have been made on the utilization of the lignosulfonic acids in sulfite waste liquor. These studies were made necessary by widespread demands for the elimination of stream pollution. Recovery of chemical values from sulfite waste liquors, which hitherto could not be used even as a fuel, supplied the economic drive for these investigations.

One of the commercially feasible processes for the utilization of sulfite waste liquor is the production of vanillin by alkaline oxidation of the lignosulfonic acids. Because of the acid nature of the sulfite waste liquor, the cost of the caustic becomes the predominant item of expense for this oxidizing operation. The alkaline nature of kraft and soda black liquors offers the possibility for the elimination or reduction of this item in an alkaline oxidation. Furthermore, the practice of recovering heat and chemical values from the alkaline black liquors can still be carried out on the spent oxidation mixture.

Considerably higher yields of vanillin may be obtained by oxidizing the sulfite waste liquors with nitrobenzene in an alkaline medium. This method also affords the simultaneous preparation of nitrobenzene reduction products.

It is readily apparent that the above considerations make the study of the oxidation of kraft black liquors with nitrobenzene of academic and, possibly, commercial interest.

## HISTORICAL REVIEW

Lignin material was first oxidized with nitrobenzene by Schulz (1) in 1940 when he obtained a patent for the superatmospheric (200° C.) oxidation of lignin-containing materials with nitrobenzene in caustic solution, giving 8-10% yields of vanillin based on the sulfite waste liquor solids. In the same year Freudenberg, Lautsch, and Engler (2) demonstrated that spruce lignin (cuproxan and Willstätter lignin), lignosulfonic acid, and sprucewood yield up to 25% (on the lignin basis) of vanillin under somewhat milder conditions (160° C.). Hibbert and co-workers (3) confirmed the results of Freudenberg and extended this process to hardwoods, cornstalks, corncobs, rye straw, and bamboo. A combined yield of 40-45% of vanillin and syringaldehyde (1:3 ratio) was obtained from hardwoods. Pearl and Lewis (4) made an extensive study of the variables of the reaction of nitrobenzene with sulfite waste liquor at both atmospheric and superatmospheric pressures, including the investigation of the nitrobenzene reduction products.

Although the above nitrobenzene process is of rather recent interest, the oxidation of sulfite waste liquor was accomplished as early as 1898 when Pollacsek (5) obtained small amounts of vanillin by the use of air and ferric chloride. In 1904, Grafe (6) produced vanillin in low yields by heating sulfite waste liquor with lime at 180° C. It was not until 1928 that higher yields (up to 20%) were obtained when Kürschner (7) modified the latter process, using potassium hydroxide and a stream of air. Numerous modifications of this process followed, including two commercially feasible processes: the Marathon-Howard process (8), and the Hibbert-Tomlinson process (9).

Until 1928, vanillin was obtained only from sulfonated lignin. In that year Pauly and Feuerstein (10) disclosed that vanillin was produced by mild oxidation of lignin in a variety of materials including grasses, straw, and wood, without previous sulfonation of the lignins. Among the oxidizing agents used were ozone and acetic acid, chromic and acetic acids, and chromic and sulfanilic acids.

Although Schulz' patent (1) on the nitrobenzene oxidation of sulfite waste liquor incorporated all lignin-containing materials, the only known attempt to oxidize the lignin in kraft black liquor was made by Breneck and Müller (11). By heating one liter of kraft black liquor for 30 hours at 103° C. in the presence of a stream of oxygen, 1.2 grams of pure vanillin were obtained.

At the present time, the organic materials in kraft black liquor are used mainly as a fuel. However, numerous processes have been developed for the recovery of alkali lignin, tall oil, and organic acids (acetic and formic) from black liquors. Processes for the destructive distillation of black liquors lead to the recovery of methanol, acetic acid, oxalic acid, acetone, higher ketones, oils, and tars.

### PRESENTATION OF PROBLEM

In view of the considerations outlined in the Introduction, a fundamental study of the reaction between a kraft black liquor and nitrobenzene was to be made to determine: (1) Whether kraft black liquors can be oxidised with nitrobenzene to vanillin or similar guaiacyl products, (2) the optimum conditions for the oxidation, and (3) the nature and yield of the various products of oxidation.

#### NATURE OF KRAFT BLACK LIQUOR USED

A 55-gallon drum of commercial black liquor used in this study was obtained from the Thimpany Pulp & Paper Company. The conditions under which this black liquor was prepared are listed in Table I.

The drum of black liquor was allowed to set overnight in order to permit any soaps to settle to the top. The liquor was then drawn off into 5-gallon jars which were completely filled, sealed with paraffin wax, and placed in a cold storage room. As the liquor was used, it was transferred to progressively smaller bottles. These precautions were taken to keep oxidation at a minimum. The liquor appeared to be free of tall oil soaps.

In order to cover a wider range of variables in the oxidations, a more concentrated black liquor was required. This was prepared by concentrating under reduced pressure (at 35° C.) five gallons of the original black liquor to less than half its original volume. This material was slightly sirupy in nature.

The analyses made on the liquor in accordance with Institute Method 109 are summarized in Table II. Lignin in the black liquor was calculated from the percentage of total solids and the methoxyl content of the solids, assuming that all the methoxyl was in the lignin and that the methoxyl content of the lignin was 14.5%.

TABLE I

CONDITIONS UNDER WHICH BLACK LIQUOR WAS PREPARED

Date of cook	December 15, 1947
Wood pulped	8.5 cords of 100% green jack pine
Type of digester	Direct heating rotary (1935 cu. ft. capacity)
Cooking liquor	
Dilute black liquor	178 gal.
White liquor	3822 gal. (equiv. to 3640 lb. active Na <sub>2</sub> O)
TAPPI sulfidity	25
Maximum pressure	105 lb.
Time to max. pressure	92 min.
Time at max. pressure	90 min.
Blowing characteristics	Started to blow at 66 lb. pressure with a total blowing time of 20 min.
Permanganate number of stock	20.3 (somewhat softer than for standard wrapping grade)
Black liquor sample	55 gallons drawn off directly from the diffuser

TABLE II

BLACK LIQUOR ANALYSIS

	As Received	Concentrated
Specific gravity	1.135	1.336
Solids, %	21.85	45.6
Methoxyl, %	4.17	4.28
Sulfated ash as NaOH, %	40.2	--
Organic matter, %	59.8	--
Lignin (calcd.), %	6.28	13.45
Active alkali (as NaOH), g./l.	26.9	56.1
Na <sub>2</sub> S (as NaOH), g./l.	15.8	33.0
NaOH (as NaOH), g./l.	11.1	23.1
Total alkali (as NaOH), g./l.	82.3	171.8

## STUDY OF OPTIMUM OXIDATION CONDITIONS

### PROCEDURE

#### Oxidations at Atmospheric Pressure

The kraft black liquor was placed in a three-neck flask fitted with a reflux condenser and a mechanical stirrer under a mercury seal. Stirring was started and sodium hydroxide pellets were added. The flask was then closed by a rubber stopper carrying a thermometer reaching below the surface of the reaction mixture. Nitrobenzene was added slowly through the top of the condenser. The flask was heated by means of an electric heating mantle. The mixture was brought to a gentle boil within approximately 45 minutes. Boiling and stirring were continued for the time of the experiment, and the reaction mixture was then allowed to cool to room temperature with stirring.

The alkaline reaction mixture was transferred to a continuous extractor (12) in which the unreduced nitrobenzene and its reduction products were extracted with ether. The ether-extracted alkaline solution was acidified to approximately pH 2 by slowly adding sulfuric acid with violent agitation and was then filtered or centrifuged. The amber-colored acid filtrate was extracted with ether in a continuous extractor, and the precipitate was air dried, ground to 40 mesh, and extracted with ether in a Soxhlet extractor.

The above extractions were carried to exhaustion as evidenced by the color and solids content of fresh portions of the ether extract. The average extraction was continued for 60 hours.

The ether extracts from the acid filtrate and precipitate were combined, dried with anhydrous sodium sulfate, freed of ether by distillation on a water bath, and weighed.

#### Supercritical Pressure Oxidations

These oxidations were made in a stainless steel autoclave (Parr hydrogenation apparatus) of approximately 400-ml. capacity equipped with a thermometer well, blow-off safety valve, and an exhaust valve. After the individual reactants (black liquor, sodium hydroxide pellets, and nitrobenzene) were placed in the autoclave, it was sealed with a plug bearing the valves and thermometer well. This plug was held in place and tightened by a threaded steel cap fitted with eight tightening bolts. A copper gasket was used to effect a seal. The autoclave was turned end-over-end several times to insure thorough mixing of the contents and then placed in an electrically heated rocker. Rocking was started and the temperature was gradually raised to the desired temperature in approximately 45 minutes and kept at that point for the time of the experiment. The autoclave was then allowed to cool to 50° C. with rocking, removed from the rocker, and cooled to room temperature under tap water. The exhaust valve was opened, the plug removed, and the reaction mixture was removed from the autoclave. The precipitate in the reaction mixture was centrifuged or filtered through a sintered-glass funnel, washed with a small amount of water, and extracted with ether. This ether extract was combined with the ether extract obtained from the continuous

extraction of the alkaline filtrate. The reaction mixture was then treated in the same manner as described for the atmospheric pressure oxidations.

In the first twelve oxidations, ether was used to extract the acid solution and precipitate for removal of the lignin oxidation products. Beginning with Oxidation 13, benzene was used instead of ether because considerable ether was lost in the continuous extractors. In order to compare the results of the various oxidations, the yield of ether-soluble material was converted to benzene-soluble material by the following arbitrary method. The ether-soluble fractions were dissolved in acetone (5 ml. for each gram). The acetone solution was precipitated into 20 volumes of benzene by dropwise addition and constant stirring. The benzene-acetone solution was filtered and the acetone distilled off at constant volume. The acetone-free benzene solution was filtered and distilled under reduced pressure to remove benzene. The benzene-soluble fractions were weighed and their methoxyl contents were determined.

#### PRESENTATION AND DISCUSSION OF DATA

The conditions and yields of the various oxidations are presented in Table III. The yield data are reported as the percentage yield of benzene-soluble materials based on lignin\* in the black liquor and also as the percentage of methoxyl recovered in the benzene-soluble fractions. The two yield figures vary because some nonlignin substances may be benzene soluble

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\*As defined by the method of analysis on page 6. A portion of this value actually comprises lignin degradation products.

TABLE III

## SUMMARY OF SMALL-SCALE OXIDATIONS

Max. Temp., °C.	Time at Max. Temp., hr.	Benzene Solubles				
		Yield, g.	Yield (based on lignin), %	OCH <sub>3</sub> , %	OCH <sub>3</sub> , g.	OCH <sub>3</sub> recovered, %
103	8	6.91	19.4	9.70	0.67	13.0
107	8	10.69	17.4	10.9	1.17	13.2
117	8	13.38	21.6	11.1	1.49	16.8
170	3	5.26	11.4	8.18	0.43	6.4
170	3.5	3.24	18.1	11.3	0.37	14.3
170	3	4.32	24.2	10.15	0.44	17.0
170	3	5.57	31.2	12.89	0.72	27.8
170	3	6.47	36.2	10.24	0.66	25.5
170	3	5.57	31.2	11.62	0.65	25.1
170	1	5.64	31.6	10.87	0.61	23.6
200	1	4.59	25.7	9.54	0.44	17.0
200	1	4.40	30.8	7.09	0.31	15.0
200	3	2.45	13.7	9.55	0.23	8.9
200	3	1.43	10.0	4.37	0.06	2.9
200	1	2.38	16.5	2.85	0.07	3.4
200	3	2.06	14.4	2.32	0.05	2.4
170	3	4.11	23.0	12.07	0.50	19.3
140	6	5.01	28.1	9.66	0.48	18.5
105	8	7.41	20.8	9.49	0.70	13.6
170	1	9.91	21.5	8.17	0.81	12.1

and demethylation of lignin degradation products may occur under some oxidizing conditions.

The yield of benzene-soluble fractions was believed to be the most desirable means of determining the degree of oxidation of the lignin and afforded the best comparison of the various oxidations. Previous investigators in the field of lignin oxidation were mainly interested in high yields of vanillin. However, since this was to be a fundamental study of the reaction between nitrobenzene and kraft black liquor, it was desirable to obtain a high yield of a fraction which contained all of the related guaiacyl compounds. After obtaining the highest possible yield of benzene-soluble fractions, the second part of this study was to determine the exact nature and yields of the individual constituents in the benzene-soluble materials.

As a starting point, the first oxidation was based on Schulz' (1) proportions for sulfite waste liquor with a slight excess of water which was due to the concentration of the black liquor as received. This atmospheric pressure oxidation resulted in a yield of 19.4% of benzene-soluble products. In Oxidation 3, the concentrated black liquor was used without added alkali. This resulted in a yield of 17.4%. The yield was brought up to 21.6% (Oxidation 4) by doubling the nitrobenzene ratio.

Oxidation 5 was patterned from Oxidation 3 and tested the behavior of the reaction under superatmospheric pressure. This resulted in lowering the yield from 17.4 to 11.4%. However, when Oxidation 1 was repeated at 170° C. with no additional alkali, the yield was only slightly decreased in Oxidation 6 and considerably increased to 24.2% in Oxidation 7 when the same ratio of alkali was used.

TABLE III

SUMMARY OF SMALL-SCALE OXIDATIONS

Oxidation	Black Liquor, g.	Lignin, g.	H <sub>2</sub> O in Black Liquor, g.	NaOH in Black Liquor, g.	NaOH added, g.	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> , g.	Reactant ratio based on 1 part lignin,		
							C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	NaOH	H <sub>2</sub> O
1 <sup>a</sup>	568	35.7	443	5.6	42.0	42.0	1.2	1.3	12.4
3 <sup>b</sup>	443	61.2	242	7.7	0	72.0	1.2	0.1	4.0
4 <sup>b</sup>	443	61.2	242	7.7	72.0	144.0	2.4	1.3	4.0
5 <sup>d</sup>	334	46.1	182	5.8	0	54.2	1.2	0.1	4.0
6	284	17.8	222	2.8	0	21.0	1.2	0.1	4.0
7	284	17.8	222	2.8	21.0	21.0	1.2	1.3	12.4
8	284	17.8	222	2.8	21.0	42.0	2.4	1.3	12.4
9	284	17.8	222	2.8	21.0	63.0	3.6	1.3	12.4
10	284	17.8	222	2.8	42.0	63.0	3.6	2.5	12.4
11	284	17.8	222	2.8	42.0	63.0	3.6	2.5	12.4
12	284	17.8	222	2.8	42.0	63.0	3.6	2.5	12.4
13	227	14.3	177	2.2	42.0	126.0	8.8	3.1	12.4
14	284	17.8	222	2.8	42.0	63.0	3.6	2.5	12.4
15	227	14.3	177	2.2	42.0	126.0	8.8	3.1	12.4
16	227	14.3	177	2.2	84.0	126.0	8.8	6.0	12.4
17	227	14.3	177	2.2	84.0	126.0	8.8	6.0	12.4
18 <sup>c</sup>	--	17.8	222	--	23.8	42.0	2.4	1.3	12.4
19	284	17.8	222	2.8	21.0	42.0	2.4	1.3	12.4
20	568	35.7	443	5.6	42.0	84.0	2.4	1.3	12.4
21 <sup>b</sup>	334	46.1	182	5.8	54.2	108.4	2.4	1.3	4.0

<sup>a</sup>Schulz' proportions

<sup>b</sup>Concentrated black liquor

<sup>c</sup>Indulin A used instead of black liquor

Because of the fact that inorganic reducing substances, which may be more easily oxidized than lignin, are present in kraft black liquor, it was decided to determine the effect of increasing the nitrobenzene ratio. Since Oxidation 7 gave the best yields thus far, Oxidations 8 and 9 were patterned after it. By doubling the nitrobenzene ratio in Oxidation 8, the yield was increased to 31.2%. In Oxidation 9, a threefold increase of nitrobenzene resulted in a 36.2% yield with a somewhat lower methoxyl content.

In Oxidation 10, it was felt that perhaps a further increase in yield could be obtained by increasing both the alkali and the nitrobenzene ratio. This resulted in a lower yield (31.2%).

Oxidation 11 indicated that, under the assigned conditions, the reaction is completed during the first hour. This is evidenced by the fact that no decrease in yield was obtained by carrying out the reaction for one hour instead of the previously assigned three hours used in Oxidation 10.

Since the oxidations carried out at 170° C. gave considerably higher yields than the atmospheric oxidations, a further study was made on the effect of using even more drastic conditions. Oxidations 12 to 17 inclusive were carried out at 200° C. In general, these oxidations resulted in much lower yields and considerable demethylation of the benzene-soluble materials took place. The acid filtrates before and after benzene extraction had a much deeper amber color and the weight of precipitated lignins on acidification of the alkaline reaction mixtures was much less, both indicating

considerably more degradation of the lignin took place but to an insufficient degree to make it benzene soluble.

The effect of ingredients other than lignin in black liquor was studied in Oxidation 18 by substituting Indulin A, a purified pine kraft lignin prepared commercially by the West Virginia Pulp and Paper Company, for kraft black liquor under the conditions of Oxidation 8. This resulted in a much lower yield of 23.0%, as compared with 31.2% in Oxidation 8.

To test the effect of a temperature between 110 and 170° C., Oxidation 8 was repeated at 140° C. for six hours in Oxidation 19. A slight lowering of yield (to 25.1%) was observed.

Since only a few oxidations were made under atmospheric conditions, Oxidation 8 was repeated under atmospheric conditions in Oxidation 20. This oxidation also afforded a comparison with Oxidation 1, in that the nitro-benzene ratio was doubled, and with Oxidation 4 which showed the effect of increasing the water ratio. The yield of 20.5% was much lower than that from the superatmospheric Oxidation 8 and was in the same range as Oxidations 1 and 4. Since the yield in Oxidation 4 was the highest of the atmospheric pressure oxidations, this oxidation was repeated at 170° C. in Oxidation 21, whereupon the same yield was obtained.

It was impossible to make a thorough study of all the variables of this reaction. That would have necessitated several hundred oxidations. The heterogeneous nature of black liquor predisposes it to all sorts of simultaneous side reactions.

EXTRACTION OF BLACK LIQUOR

To determine the nature of the ether- and benzene-soluble materials present in black liquor before oxidation, nine liters of kraft black liquor, as received, were extracted with ether in a continuous extractor. The ether extract was dried with anhydrous sodium sulfate, and the ether was distilled to give 30.34 grams (3.37 grams per liter of black liquor) of an ether-soluble oil with a strong mercaptan odor. The oil was further distilled under reduced pressure. The residue consisted of 8.23 grams (0.91 gram per liter) of a yellow-brown solid. The distillate was a red liquid. The yellow-brown solid was dissolved in a small quantity of ether. A white crystalline material failed to dissolve and was filtered. The crystals, on being freed of ether turned into an oil. The oil turned into a cream-colored powder, which still had a mercaptan odor, after long standing.

The ether-extracted kraft black liquor was devoid of any odor after the extraction. However, after several months of standing, a slight kraft odor was again observed. A 500-ml. aliquot of the extracted black liquor was acidified with sulfuric acid until the pH was approximately 2. The brown precipitate was filtered, dried, ground to a fine powder, and extracted with ether in a Soxhlet extractor. The light brown filtrate was extracted with ether in a continuous extractor.

The ether extracts from the precipitate and filtrate were combined and dried with anhydrous sodium sulfate, and the ether was distilled on a water bath. The yield of ether-soluble oil was 12.23 grams. The ether-soluble materials were converted to a benzene-soluble fraction by

dissolving the ether-soluble oil in 122 ml. of acetone. A small amount of sulfur was filtered and the acetone solution was precipitated dropwise into 2440 ml. of benzene with rapidly stirring. The red solution was decanted from the precipitated tar, and the acetone was removed by distillation at constant volume. The acetone-free solution was again decanted and the benzene was distilled under reduced pressure. The yield of benzene-soluble materials was 10.33 grams (28.9% based on the lignin). The methoxyl content was 10.26%. This represents a recovery of 20.5% of the original methoxyl in the black liquor.

## LARGE-SCALE OXIDATION

### OXIDATION PROCEDURE

In order to provide for a larger sample of benzene-soluble materials which would permit the identification of products formed in extremely low yields, a large-scale oxidation was carried out under the conditions giving the best yields among the small-scale oxidations (Oxidation 8).

This oxidation was made in a stainless steel, cylindrical, horizontal rotary autoclave (29 inches long and 9.5 inches in diameter) having a capacity of 33.7 liters. One head of the autoclave was equipped with a relief valve, a pressure gage, and thermometer well. The other head contained a safety valve. In the center of the cylindrical body was a four-inch charging hole with a plug. The autoclave was heated by six gas jets. It was suspended on and driven by two drive shafts. The rate of rotation was 20 revolutions per hour.

The autoclave was charged with 20 liters of kraft black liquor, 1680 grams of sodium hydroxide pellets, and 2780 ml. of nitrobenzene (3360 grams). The charging hole plug was screwed on and rotation was started. The contents were heated to 170° C. in 45 minutes; this temperature was maintained for 3 hours. Heating was then discontinued, and the autoclave and contents were allowed to cool to room temperature while rotating. The rotation of the autoclave was stopped when the relief valve was in the uppermost position. No gas was evolved when the relief

valve was opened. The autoclave was turned through 180°, and the contents were emptied through the relief valve after the charging plug was removed. In contrast to the results obtained in Oxidation 8, the reaction mixture had a nitrobenzene odor and did not contain a precipitate. The last traces of the reaction mixture were washed out of the autoclave with a stream of water.

## SEPARATION AND ANALYSES OF OXIDATION PRODUCTS

### Extraction of Nitrobenzene and Reduction Products

The alkaline reaction mixture and washings (a volume of 27 liters) were filtered and transferred to a large continuous extractor in which the nitrobenzene and its reduction products were removed with benzene. The benzene extract was as dark as the reaction mixture and partially emulsified during the early part of the extraction. This benzene extract was placed in a series of 2-liter separatory funnels. After settling overnight, no line of separation could be observed, even with the aid of a beam of light. The two layers were separated by trial and error in the following manner. An amount of solution believed to be free of benzene was drawn off and extracted with fresh benzene whereupon two layers could be observed and separated. This lighter colored benzene extract was added to the portion believed to consist wholly of an emulsion. The portion of the original benzene extract which was believed to consist of benzene extract only was extracted with 5% sodium hydroxide. After a number of such extractions, the benzene extract was freed of emulsion and resolved into a distinct benzene-soluble extract. The 5% sodium hydroxide-soluble materials were combined with the benzene-extracted

reaction mixture. The benzene extract of nitrobenzene and its reduction products comprised a volume of 14 liters.

#### Extraction of Lignin Oxidation Products

The benzene-extracted alkaline reaction mixture was acidified to approximately pH 2 by slowly adding concentrated sulfuric acid with rapid stirring. Because of foaming and in order to avoid a great temperature rise, the acidification was accomplished by periodic additions of sulfuric acid. After two days the desired pH was attained.

The acidified mixture was centrifuged in a basket centrifuge. The acid filtrate was extracted to exhaustion with benzene in continuous extractors. Upon completion of the extraction, the benzene was distilled under reduced pressure and 59.7 grams of a brown benzene-soluble oil was obtained.

The precipitate of lignin and sodium sulfate obtained by centrifuging the acidified reaction mixture was air dried and ground in a Wiley mill to pass a 40-mesh screen. The tan powder was extracted with benzene in three large Soxhlet extractors. The benzene extract was distilled under reduced pressure to yield 245.9 grams of a brown benzene-soluble oil. The combined yield from the filtrate and precipitate was 305.6 grams.

Crystals formed in both the benzene-soluble fractions. These were isolated by dissolving the benzene-soluble materials in the minimum quantity of ethanol, filtering the insoluble crystals, and washing them well with ethanol. These yellow crystals had a melting point of 111° C., burned with a blue flame, and evolved sulfur dioxide. This identified them

as rhombic sulfur. The sulfur amounted to 26.3 and 25.0 grams of the benzene-soluble fraction from the filtrate and precipitate, respectively.

Because of the similarity in color and physical appearance of the benzene-soluble fractions from the filtrate and precipitate, it was felt that no separation of components was made by the separate extractions. Accordingly, the ethanol solutions of the benzene-soluble products were combined and the ethanol was distilled under reduced pressure. The combined yield of benzene-soluble fractions was 251.2 grams, representing a yield of 17.6% based on the lignin in the black liquor. The methoxyl content was 10.5%, which represents a recovery of 13.1% of the original methoxyl content of the black liquor. The similar small-scale Oxidation 8 gave a benzene-soluble yield of 31.2% and a methoxyl recovery of 27.8%.

A small portion of the waste benzene-extracted acid filtrate was tested by extracting with ether. The ether layer became yellow. On warming another portion of the waste filtrate, sulfur dioxide was evolved.

Since there was a possibility that aldehydes were retained as bisulfite addition products, the benzene-extracted acid filtrate was boiled under reflux in the presence of a slow stream of air to remove sulfur dioxide. During the refluxing, a greenish-brown precipitate was formed. At the same time a yellow-white solid began to collect in the condenser. The gas evolved had a sulfur dioxide and mercaptan odor and gave a sulfur dioxide test with nickelous hydroxide paste and also with filter paper moistened with iodine solution.

The refluxing was changed to a steam distillation to collect the steam distillable material. After several days of steam distillation, the distillate still had a sulfur dioxide and mercaptan odor. The material which steam distilled was sulfur. The steam distillate was strongly acid (pH 2).

The refluxed solution was filtered and 30.2 grams of a greenish-brown ligninlike precipitate was obtained. The filtrate was extracted with ether in a continuous extractor. The red ether extract was dried with anhydrous sodium sulfate and the ether removed by distillation in a water bath. The yield of ether-soluble materials from the filtrate was 117.5 grams.

After the benzene extraction, the precipitated lignins obtained on acidification of the oxidation reaction mixture were air dried, reground in a Wiley mill to break up agglomerated clumps, and extracted with ether in the large Soxhlet extractors. The ether extract, after treatment as above, yielded 146.6 grams of ether-soluble oil.

The ether-soluble materials from the precipitate and filtrate appeared to be similar. They were dissolved in ethanol and the ethanol solutions were combined. After the ethanol was distilled under reduced pressure, 263.5 grams of a red-brown, ether-soluble oil remained. The methoxyl content of the ether-soluble fractions was 6.1%.

The benzene- and ether-extracted precipitated lignin had a methoxyl content of 3.2%. An aliquot of the extracted acid filtrate was taken to dryness. The methoxyl content of the solids was 0.14%. The

methoxyl balance showing the distribution of the original 206.8 grams of methoxyl in the black liquor is summarized in Table IV.

TABLE IV  
METHOXYL DISTRIBUTION AFTER OXIDATION

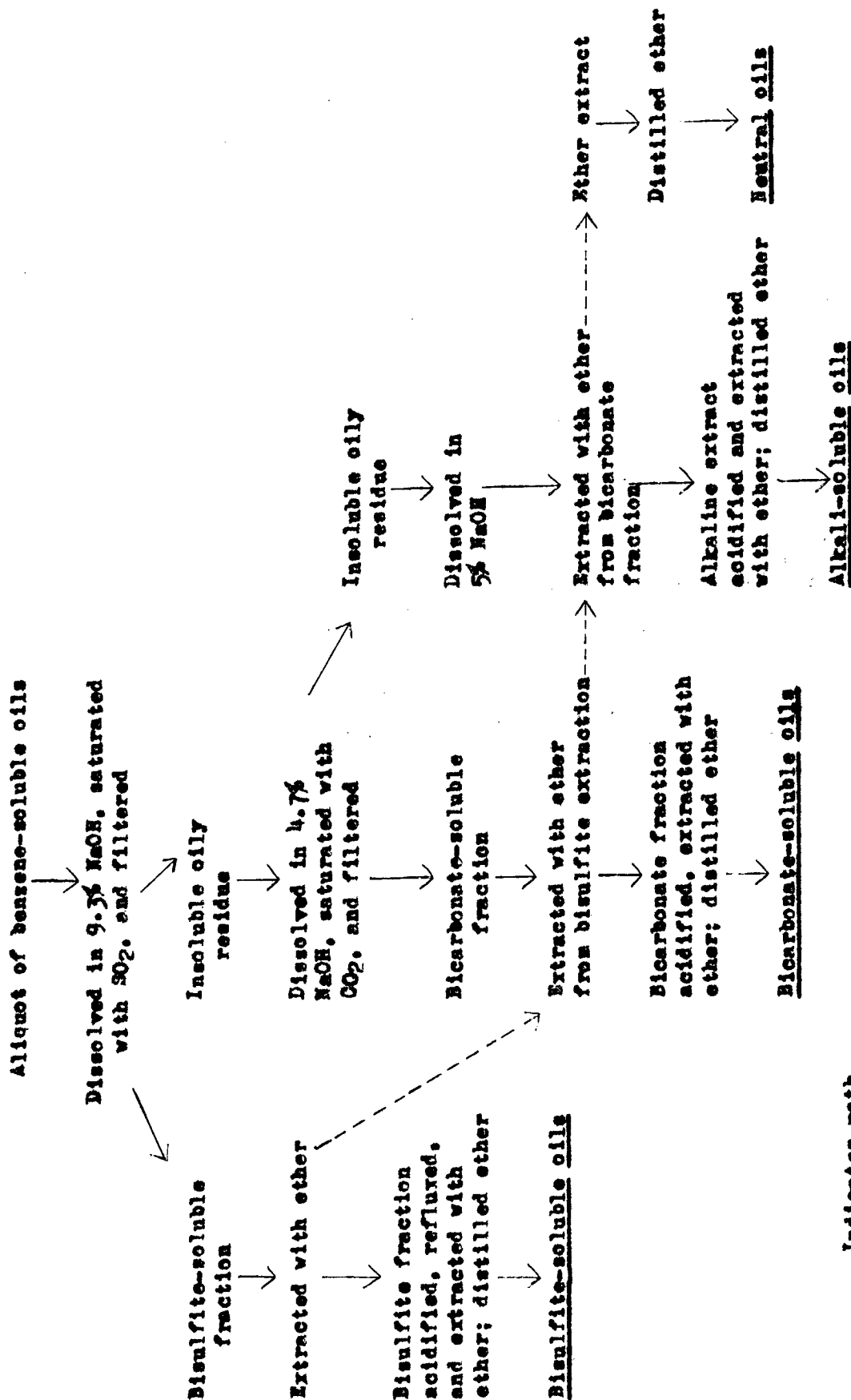
Fraction	Methoxyl, %	Methoxyl, g.	Percentage of Original
Benzene-soluble	10.84	27.2	13.1
Ether-soluble	6.14	16.2	7.8
Precipitated lignins	3.19	158.3	76.5
Acid filtrate	0.14*	4.5	2.3
Total	--	206.3	99.7

\*Based on solids

Class Separation of Benzene-Soluble Materials

The various steps in the class separations, which are described in more detail below, are summarized in Figure 1.

A 101.5-gram aliquot (40.4%) of the benzene-soluble materials extracted from the acidified reaction mixture was dissolved by triturating and stirring in small portions of 9.3% sodium hydroxide solution in an ice bath until the benzene-soluble materials were completely dissolved. A volume of 350 ml. of the alkali, which was equivalent to a 21% sodium bisulfite solution when saturated with sulfur dioxide, was required to effect solution. This alkaline solution was saturated with sulfur dioxide in an ice bath. The cloudy yellow bisulfite extract was decanted from the



-----Indicates path of same ether extract

FIGURE 1

Class Separation of Benzene-Soluble Materials

dark viscous material which precipitated on acidification. The precipitate was redissolved in 500 ml. of 9.3% sodium hydroxide in the same manner and saturated with sulfur dioxide. The operation was repeated for a third time, again requiring 500 ml. of alkali. The three bisulfite-extracted fractions were combined and extracted three times with 150-ml. portions of ether in an attempt to remove materials which did not react with bisulfite but were water soluble.

The bisulfite extract was acidified with 90 ml. of concentrated sulfuric acid, which was added dropwise with agitation. A dark oil was liberated. The acidified solution was boiled under reflux while a slow stream of air was passed in. The refluxing was maintained for five minutes after the solution reached the boiling point. Sulfur dioxide and some material with a mercaptan-like odor was still being evolved, but heating was discontinued. The gaseous odor was similar to that evolved during the steam distillation of the acidified reaction mixture filtrate. The clear yellow acid solution was decanted from the dark oil, saturated with sodium chloride, and extracted with ether in a continuous extractor. The ether extract was dried with anhydrous sodium sulfate and filtered, and the ether was removed by distillation in a water bath. The dark oil which separated on acidification was not appreciably soluble in ether and was, therefore, dissolved in ether-ethanol. This solution was distilled under reduced pressure with the above ether-soluble materials to remove the ethanol.

The yield of bisulfite-soluble materials was 35.58 grams, and the methoxyl content was 15.7%.

The tarry material, which was insoluble in 21% sodium bisulfite solution, was extracted with a saturated sodium bicarbonate solution in the following manner. Sodium hydroxide solution (4.7%) was added to the material in small portions. After triturating and stirring, the saturated alkaline solution was poured off and the operation repeated with fresh portions of alkali until the material was completely dissolved. Six hundred and ten ml. of alkali were required to effect complete solution. This alkaline solution was placed in an ice bath and saturated with carbon dioxide. The clear golden extract was filtered from the brown amorphous precipitate which became tarry on the filter paper. A second bicarbonate extraction requiring 580 ml. of 4.7% sodium hydroxide solution was made on the precipitate in the same manner. The precipitate was filtered and washed with an 8% sodium bicarbonate solution. The two bicarbonate extracts were combined and extracted with the ether extract obtained from the bisulfite-soluble materials. The ether extract became a lighter red and was again extracted with a small, fresh portion of 8% sodium bicarbonate solution which was combined with the other bicarbonate-soluble materials. The bicarbonate-soluble fraction was then extracted with a fresh portion of ether.

The bicarbonate extract was acidified by the dropwise addition of approximately 50 ml. of concentrated sulfuric acid with stirring to liberate carbon dioxide. As carbon dioxide was liberated, a dark oil separated and the solution became lighter in color. The carbon dioxide-free solution was poured off, saturated with sodium chloride, and extracted

with ether in a continuous extractor. The ether extract was distilled in a water bath to remove the ether. The dark oil was dissolved in ethanol. The ethanol solution was combined with the ether-bicarbonate soluble materials and the ethanol was distilled off under reduced pressure.

The yield of bicarbonate-soluble materials, which had a methoxyl content of 8.2%, was 22.86 grams.

The tarry precipitate from the bicarbonate extraction was dissolved in 450 ml. of 5% sodium hydroxide solution in the manner previously described. The resulting alkaline solution was extracted with the ether extract from the bicarbonate extraction followed by three fresh 100-ml. portions of ether. The combined ether extracts were extracted with 50 ml. of 5% sodium hydroxide solution, which was combined with the other phenolic extract. The remaining ether extract represented the neutral materials.

The alkaline solution of phenolic materials was acidified with 12 ml. of concentrated sulfuric acid. The dark solution became light brown and a dark oil separated. The acidified solution was filtered, saturated with sodium chloride, and extracted with ether in a continuous extractor. The dark oil was dissolved in ethanol and combined with the ether extract; the solvents were removed by distillation under reduced pressure.

The yield of 5% sodium hydroxide-soluble materials was 25.58 grams. The methoxyl content was 16.0%.

The ether extract of neutral materials was dried with anhydrous sodium sulfate and the ether was removed by distillation. The yield of neutral materials was 1.53 grams. This contained, in part, a small amount of the nitrobenzene reduction products which were not previously extracted.

The converted total yields of the above materials are summarized in Table V.

TABLE V

COMPOSITION OF BENZENE-SOLUBLE MATERIALS

Fraction	Yield, g.	Methoxyl, %	Yield (based on Benzene- soluble Fractions), %	Yield (based on Lignin), %
Bisulfite-soluble	88.0	15.7	35.1	6.2
Bicarbonate-soluble	56.5	8.2	22.6	4.0
Alkali-soluble	63.2	16.0	25.2	4.4
Neutral	3.8	--	1.5	0.3
Total	211.5	--	84.4	14.9

Analysis of Bisulfite-Soluble Fraction

The bisulfite-soluble oils were distilled under reduced pressure. A yellow syrupy material (3.94 grams) distilled at 65-72° C./0.04 mm. while the bath temperature was maintained at 140° C. Raising the bath temperature to 180° C. failed to produce any additional distillate. The yellow syrup consisted of a few crystals, which were identified as sulfur, and a yellow oil. This oil was insoluble in water, petroleum ether, and ligroin. Attempts

to obtain a crystalline product from dilute ethanol, ether-petroleum ether, and benzene-ligroin mixtures failed. The oil was soluble in bisulfite but failed to yield crystalline derivatives with hydroxylamine, phenylhydrazine, and 2,4-dinitrophenylhydrazine. Oily derivatives were obtained except with the latter reagent, in which case no reaction was believed to have taken place.

The bisulfite-soluble undistillable materials were taken up in absolute ether for transfer to a sublimation apparatus. The material was only slightly soluble in the ether. Hence, the remainder of the material was dissolved in absolute ethanol. When the alcohol solution was combined with the ether solution, a light brown ligninlike precipitate was formed. This was filtered and washed with ether. On drying, the precipitate (5.55 grams) turned into a dark tarry material. The light brown amorphous character was restored on the surface of the tar when the material was resuspended in ether.

The solvent was distilled from the filtrate under reduced pressure. The brown oily product (20.05 grams) was sublimed in an oil bath (90° C.) under a pressure of 0.04 mm. After a 24-hour sublimation period, 0.4 gram of a white solid slightly moist with oil was obtained. A small portion of the solid was placed on a porous plate, briefly washed with ether, and the melting point determined. The white crystals melted at 203° C., which was indicative of vanillic acid. The white solid was

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\*All melting points are uncorrected and were determined on a Fisher-Johns melting point apparatus unless otherwise indicated.

completely sublimed from the residue after 32 days of continuous heating. During the latter stages of the sublimation, the bath temperature was raised to 100° C. and then to 120° C. to speed the removal of the solid. The yield of sublimate was 5.76 grams.

In order to separate the crystalline portion of the sublimate from the oil, the sublimate was treated with portions of hot water (70° C.) until the clear, slightly yellow, aqueous solution was no longer very acidic. The remaining insoluble oil was dissolved in ether and extracted with small portions of 5% sodium bicarbonate solution. The bicarbonate extract was acidified and a brown oil separated. The oil was filtered and the yellow filtrate was extracted with ether. On distillation of the ether, crystals melting at 195-208° C. were obtained. Crude crystals formed in the brown oily precipitate. These were removed by treating as previously noted with hot water, leaving behind a red-brown oil. The ether extract of the bicarbonate-insoluble oil was combined with the above oil. Distillation of the ether left 1.72 grams of a red-brown oil. The yield of practically pure crystalline material was 7.04 grams.

The aqueous solution of the crystalline material was concentrated to a small volume and allowed to cool. White needles melting at 193-203° C. were filtered. Recrystallizations to a constant melting point from water and ethanol and a single carbon black treatment yielded pure vanillic acid melting at 207-208° C. (capillary). There was no depression in a mixed melting point determination with authentic vanillic acid.

Analysis. Calculated for vanillic acid,  $C_8H_8O_4$ :  $CH_3O$ , 18.44%.  
Found:  $CH_3O$ , 18.38%.

In order to determine the nature of the 1.72 grams of oil which sublimed with the vanillic acid, a methoxyl determination was made. A methoxyl content of 17.52% indicated that the material originated from the lignin. Further analysis indicated the presence of sulfur in the amount of 1.45%. Since elemental sulfur was previously found in the benzene-soluble fraction, the oil was treated with carbon disulfide. The oil, freed of the carbon disulfide extract, still gave a positive test for sulfur. The sulfur content of the oil indicated that, if a simple sulfur derivative of a guaiacyl compound was present, it represented only 10% of the oil. Since a compound of this type would contribute greatly to the understanding of the chemistry of the kraft process, additional tests were made on the oil.

In the mercaptan test with lead acetate, a voluminous yellow precipitate was obtained. However, negative tests for mercaptans were obtained with sodium nitroprusside and mercuric oxide. The oil formed an oily derivative with 2,4-dinitrochlorobenzene. On oxidation of this oily derivative with 3% potassium permanganate solution, a small amount of tan powdery crystals, melting at 76-85° C., was obtained. A similar tan precipitate was obtained by oxidizing the original oil which contained sulfur.

The test for sulfones was doubtful. The fumes obtained on acidification of the melt from the sodium hydroxide fusion of the oil decolorized iodine paper but failed to give the sulfur dioxide test with nickelous hydroxide paste.

The following miscellaneous tests were performed on the oil. Active unsaturation was indicated since the oil decolorized potassium permanganate solution and bromine in glacial acetic acid. The compound gave a tan precipitate on treatment with ferric chloride solution. With concentrated sulfuric acid, it formed a deep red color. The presence of a carbonyl group was doubtful, since only an orange solution instead of a precipitate was obtained with 2,4-dinitrophenylhydrazine. A gummy derivative, which was only slightly soluble in ethanol, was obtained with 3,5-dinitrobenzoyl chloride. On attempted recrystallization of the derivative from dioxane-ethanol, an oil was obtained.

#### Isolation of Vanillin

In an analogous qualitative large-scale oxidation in which a portion of the oxidized kraft black liquor was lost during the steam distillation of the acidified reaction mixture, a bisulfite-soluble fraction was obtained in a similar manner. However, in this case the acidified bisulfite extract was boiled under reflux for several days without completely removing the sulfur dioxide and mercaptan odor. The acid solution was then saturated with sodium chloride and extracted to exhaustion with ether in a continuous extractor.

The ether-extracted acid solution retained a golden color. In order to determine the nature of the materials which were not ether extractable, the acid solution was distilled to dryness. The yellow inorganic salts, which had a vanillin odor, were extracted with ethanol. The yellow alcoholic extract was concentrated to a small volume and chilled.

An orange-red oil separated. Water was added to the remaining ethanol solution to precipitate more oil. Further concentration of the dilute ethanol solution resulted in the recovery of all the material as an oil. After setting for days, some crystals were formed in the oil. An attempt was made to remove the oil by recrystallizing the material from ether-ligroin without any success.

The oily residue (2.45 grams) was treated with hot water. The aqueous solution became yellow, and the red oil remained insoluble. The aqueous solution was decanted, and the oil was treated with more water until further solution did not take place. The yellow aqueous extracts were combined, concentrated to a smaller volume, and chilled. Crystal formation did not occur even after further concentration. The aqueous solution was frozen. On melting, a small amount of yellow crystals were formed. While filtering the crystals under reduced pressure, white needles began to form in the filtrate. The filtrate was chilled and filtered. The white crystals melted at 80° C. and were recrystallized from ligroin by dissolving in ether, adding ligroin, and distilling the ether. Crystals were not obtained until the ligroin was almost completely distilled. Further recrystallizations were made from water. The pure white needles formed an asbestoslike mat on filtering, melted at 80-80.5° C. (capillary), and did not depress a mixed melting point with authentic vanillin. The 2,4-dinitrophenylhydrazone melted at 269-270° C. (capillary) and gave no depression in a mixed melting point with the hydrazone prepared from authentic vanillin. The estimated yield of vanillin from the oxidation was 3.7 grams.

Analysis. Calculated for vanillin,  $C_8H_8O_3$ : C, 63.16%; H, 5.26%.  
Found: C, 63.24%; H, 5.50%.

Analysis of Bicarbonate-Soluble Fraction

Since Pearl (16) found that the lead salt of vanillic acid was soluble when an aqueous solution of acidic materials was treated with neutral lead acetate, this technique was applied to the separation of the above fraction. The oily bicarbonate-soluble fraction was triturated and stirred with a liter of hot water. The bright yellow aqueous solution was poured off and the oily residue was again treated in the same manner with smaller portions of hot water until the aqueous extract had practically no color. The hot aqueous extract, consisting of approximately three liters, was filtered and the hot filtrate was treated with an excess of saturated neutral lead acetate solution. The curdy yellow precipitate which formed was set aside to settle overnight at room temperature. The yellow precipitate of lead salts (Fraction B) was filtered and washed thoroughly with hot water. The combined filtrate and washings (Fraction A) were saturated with hydrogen sulfide and then boiled to remove excess hydrogen sulfide. The precipitated lead sulfide was filtered and washed with hot water. The colorless filtrate and washings, while being concentrated to a smaller volume, became slightly amber in color. On cooling, a small amount of brown oil separated. The cool solution was acidified with sulfuric acid, saturated with sodium chloride, and extracted with ether. The light yellow ether extract was dried with anhydrous sodium sulfate and filtered, and the ether was removed by distillation. The yield of the brown oil (Fraction A) was 4.05 grams.

The above and succeeding steps in the separation of the bicarbonate-soluble materials are schematically outlined in Figure 2.

The precipitated lead salts (Fraction B) were suspended in water, acidified with sulfuric acid, and extracted with ether. The ether extract was dried and distilled, and 2.16 grams of a red-brown oil (Fraction B) were recovered.

The hot water-insoluble oil (Fraction CDE) was dissolved in 100 ml. of ethanol and precipitated into 3 liters of water. The yellow colloidal solution was clarified by adding an additional 25 ml. of ethanol and was then treated with an excess of saturated neutral lead acetate solution. The yellow-brown precipitate (Fraction D) was allowed to settle, filtered, and washed with water. The combined filtrate and washings were distilled in order to remove the ethanol. The precipitate (Fraction E) was filtered and washed with water. Fraction C consisted of the filtrate and washings.

The soluble lead salts of Fraction C were treated in the manner described for Fraction A. The aqueous solution of the lead-free material was concentrated and cooled. Since crystallization did not take place, the solution was further concentrated until the previously colorless solution began to turn yellow. The solution was acidified with sulfuric acid, saturated with sodium chloride, and extracted with ether. The yellow ether extract was dried with anhydrous sodium sulfate, and the ether was distilled. The yield of a red-brown viscous oil was 0.58 gram.



The yellow-brown precipitate (Fraction D) was suspended in water and treated with sulfuric acid. A heavy dark tar separated. The mixture was extracted with ether. Since the tar was not very soluble in ether, it was dissolved in ethanol. The ether and alcohol extracts were combined, and the solvents were distilled under reduced pressure. The yield of a black tar was 9.57 grams.

Fraction E was treated in the same manner with the exception that the extraction was made with ether alone. The ether extract was dried with anhydrous sodium sulfate, and the ether was distilled. Fraction E consisted of 2.47 grams of a dark oil.

Fraction A. The brown oil (4.05 grams) containing crystals was sublimed under reduced pressure (0.07 mm.) in an oil bath maintained at 90° C. The sublimate consisted of 3.21 grams of a cream-colored crystalline solid melting at 187-192° C. after being washed with ether. The crystals were resublimed at 90°/0.04 mm. and yielded 2.94 grams of a product melting at 193-198°. The material was dissolved in water, treated with carbon black, and recrystallized to a constant melting point of 207-208° (capillary). A mixed melting point determination with authentic vanillic acid gave no depression.

Analysis. Calculated for vanillic acid,  $C_8H_8O_4$ :  $CH_3O$ , 18.44%.  
Found:  $CH_3O$ , 18.40%.

Fraction B. Upon sublimation of the 2.16 grams of red-brown oil at 100-140° C./0.06-0.08 mm., 0.68 gram of an orange oil was obtained. By repeated precipitations of an ether solution of the oil into petroleum ether,

lighter colored ether-petroleum ether soluble materials were obtained. The soluble fraction was decanted from the separated oils, concentrated, and chilled, and the oil was filtered. Concentration of the clear yellow solution to an extremely small volume failed to produce crystals. The residue free of solvent was composed of yellow crystals embedded in a yellow oily mass. The residue was redissolved in ether, a small amount of water was added, and the ether was distilled. The aqueous solution, which was strongly acid, was chilled. Crystal formation did not take place even on further concentration of the aqueous solution.

Concentration of the aqueous solution was discontinued when it was observed that the vapor was acidic and the material was apparently steam distilling. The aqueous solution was cooled and extracted with ether. The ether extract was subsequently extracted with a small volume of 5% sodium bicarbonate solution. The bicarbonate extract was acidified, extracted with ether, and the ether was distilled. The crystals were still oily. Microsublimation of the residue yielded long white needles coated with a small amount of yellow oil. The crystals melted at 201-228° C.

Fraction C. The red-brown viscous oil (0.58 gram) at 100° C./0.07 mm. yielded 0.35 gram of a yellow-green viscous solid, which was dissolved in the minimum quantity of ether. Ligroin was added to the ether solution and the ether was distilled. The ligroin solution was chilled and decanted from the oil which separated. On further concentration of the clear ligroin solution, irregularly shaped, rodlike, cream-colored crystals melting at 101-114° C. were obtained. The crystals were stirred with warm water

(approximately 70° C.). The acid aqueous solution was filtered from the oil which did not dissolve, and was chilled. The white crystals (melting point 110-123° C.) were filtered and recrystallized alternately from dilute ethanol and ligroin until a constant melting point of 129-130° C. (capillary) was obtained. Qualitative analysis of the crystals showed that neither nitrogen nor sulfur was present.

Analysis. Calculated for  $C_9H_9O_2$ : C, 72.49%; H, 6.04%.

Found: C, 72.84%; H, 6.04%.

A methoxyl content of 7.68% (single determination) was obtained using only a 2.4 mg. sample of the crystals. This determination served only as a qualitative indication of the presence of methoxyl groups, because of the error involved with such a small sample.

The neutralization equivalent of the material was determined by titrating potentiometrically a 1.976 mg. sample with 0.00227 N alkali. The neutralization equivalent was 145. Similar microtitrations, which were made on samples of benzoic and vanillic acids, indicated that the experimental error was approximately 10%. The pH of the above aqueous solution before titrating was 4.03. The end point of the titration occurred at pH 7.4 (6.00 ml. alkali). At this same point the following phenomenon took place. On addition of 0.10 ml. of alkali, the pH dropped from 7.31 to 7.13. Since this could have been a characteristic of a lactone, the solution was warmed to 60° C., whereupon the pH rose to 8.19. On cooling to room temperature (25° C.), the pH was 7.68. The pH readings obtained with subsequent additions of alkali followed a smooth curve. A similar break, which was less pronounced, occurred at pH 6.91 (5.65 ml. alkali).

A positive ferric chloride test indicated the possible presence of phenolic hydroxyl groups. In this test a green color was formed and a light brown precipitate was obtained. The solution on warming turned yellow and emitted a phosphorus-like odor. In order to account for both carboxyl and phenolic hydroxyl groups in the same molecule, it would be necessary to assign to the compound the lactone structure discussed above. However, the oxygen content did not permit the assumption of a lactone group and also a methoxyl group.

A survey of the literature disclosed no known acids having the above empirical formula and melting point. Cinnamic acid ( $C_9H_8O_2$ , m.p.  $133^\circ C.$ ) approximated the melting point and the formula weight. In a mixed melting point determination with cinnamic acid, a melting point of  $129-130^\circ C.$  was obtained. However, the unknown material failed to give the odor of benzaldehyde on boiling a dilute aqueous solution with a drop of ferric chloride solution and a drop of hydrogen peroxide solution. The test was given by the same small amount of cinnamic acid. Also, a negative test for unsaturation with bromine in glacial acetic acid was obtained for the unknown. However, a similar negative test was obtained for cinnamic acid.

Because of the small amount of material available and the uncertainty involved in micro tests, the remaining crystals were subjected to infrared absorption analysis. Similar absorption curves were determined on coumarin and cinnamic acid for comparison of groups and linkages suspected in the unknown compound. The results of the analysis of the infrared absorption curves are presented in Table VI. The unknown compound resembles cinnamic acid except for the hydroxyl group, which appears to be absent in

TABLE VI

## COMPARISON OF ANALYSIS BY INFRARED ABSORPTION

Absorption Band	Coumarin	Cinnamic Acid	Unknown, $C_9H_9O_2$
Hydroxyl group	Absent	Present (as carboxyl)	Absent
Carbonyl group	Present (as lactone)	Present (as acid, conjugation not indicated)	Present (same as cinnamic acid and at same frequency)
Unsaturated aliphatic group conjugated with another unsaturated group	Present	Present	Present (at same frequency as cinnamic acid)
Phenyl group	Present (only in one of two regions)	Appears degenerate	Identical with cinnamic acid
Lactone (assuming 4 to 6 membered ring)	Present	Absent	Absent
Anhydride	Absent	Absent	Absent
Unassigned region of 2330-2350 $cm^{-1}$	Present	Absent	Present

the unknown. It is interesting to note that the phenyl group appeared degenerate in both compounds. The suspected lactone was not indicated in the unknown, but some resemblance to coumarin was shown in the region of 2330 to 2350  $\text{cm}^{-1}$ . Since it appeared that the acidity of the unknown was not due to carboxyls, phenolic hydroxyls, or lactone formation, the anhydride region was examined. An anhydride structure also appeared to be absent. In view of the above, it is difficult to assign a definite structure to this unknown compound.

Fraction D. An attempt to sublime ( $90^{\circ}\text{C./}0.14\text{ mm.}$ ) the 9.57 grams of black tar yielded only a trace of a liquid with a plumlike odor. Distillation using an immersion distilling head at  $160^{\circ}\text{C./}0.04\text{ mm.}$  failed to produce additional quantities of the oil.

The black tar was only slightly soluble in ether but soluble in ethanol, acetone, dioxane, and glacial acetic acid. Precipitation of a glacial acetic acid solution of the tar into ice water produced a brown muddy precipitate. On filtering, a brown ligninlike powder was obtained.

Fraction E. Sublimation of this fraction (2.47 grams of dark oil) at  $120^{\circ}\text{C./}0.04\text{ mm.}$  produced 0.79 gram of a white solid admixed with a red oil. A portion of the red oil was removed by dissolving the sublimate in ether and extracting the ether solution with a small amount of 5% sodium bicarbonate solution. The bicarbonate extract was acidified and extracted with ether. Distillation of the ether produced brown oily crystals. Recrystallizations from a variety of solvents and solvent mixtures failed to produce crystals without the oil. By dissolving the crystalline residue

in a small quantity of hot water, a partial fractionation was made. The aqueous extract became richer in the crystalline material. The aqueous extract was concentrated to a smaller volume and chilled. A milky solution was formed. On chilling for a long period, the solution separated into an oil and aqueous layer. The aqueous layer was poured off and extracted with ether. A small amount of white crystals melting at 102-106° C. was obtained. These crystals were further purified by microsublimation yielding fine white needles melting at 109-111° C.

The oil which separated from the aqueous solution became crystalline on standing. These crystals were subjected to a microsublimation treatment. White crystals melting at 130-148° C. were obtained. On standing these crystals became brown. The aqueous solution of both crystalline materials was strongly acidic. Because of the extremely small yields and the failure to obtain pure products, no characterization tests were made.

#### Analysis of Sodium Hydroxide-Soluble Fraction

The 25.58 grams of oil from the above fraction were separated on the basis of solubility as follows. The oil was treated with 100-ml. portions of ether to dissolve the ether-soluble materials. The light brown flocculent material which was dispersed in the ether solution was filtered. The ether treatments were repeated until all the oil was removed from the flask. The combined precipitates were washed with ether.

The precipitate, on evaporation of the ether, became a dark tar. The tar was dissolved in ethanol, and the ethanol was distilled under reduced pressure. The 6.81 grams of ethanol-soluble tar (Fraction A) did not distill at 150° C./0.07 mm.

The residue from the ether-soluble fraction consisted of 18.87 grams of a dark viscous oil with a medicinal odor. The flask containing the oil was packed with glass wool to prevent bumping and foaming, and the oil was distilled under reduced pressure. At a bath temperature of 160° C. and a pressure of 0.22 mm., 1.63 grams (Fraction B) of light brown oil distilled. This fraction was followed by 4.35 grams (Fraction C) of a red oil which solidified into a yellow solid. Neither fraction had a constant boiling point. The bath temperature was raised to 180° C. to remove all the yellow solid. To obtain Fraction D, the residue was heated with a Bunsen flame, and an additional 1.50 grams of dark oil were obtained, using an electrically heated fractionating column. The distillation was discontinued when white fumes, indicating decomposition, were evolved. The fractionations of the sodium hydroxide-soluble materials are outlined schematically in Figure 3.

Efforts to form crystalline derivatives of the oily Fractions B and D failed. The following reagents were used: benzoyl chloride, 3,5-dinitrobenzoyl chloride (in anhydrous pyridine), and 1-naphthyl isocyanate.

The yellow solid (4.35 grams) obtained in Fraction C melted at 80-95° C., and was purified by sublimation at 80° C./0.03 mm. to yield 3.81 grams of a white solid melting at 102-112° C. Recrystallizations from dilute ethanol and ligroin yielded white needles melting at 113.5-114° C. A mixed melting point with authentic acetovanillone was not depressed. Acetovanillone benzoate was prepared by shaking with benzoyl chloride and sodium hydroxide, and the resulting derivative was recrystallized from ethanol to give long fibrous needles melting at 102° C. and not depressing a mixed melting point with authentic acetovanillone benzoate.

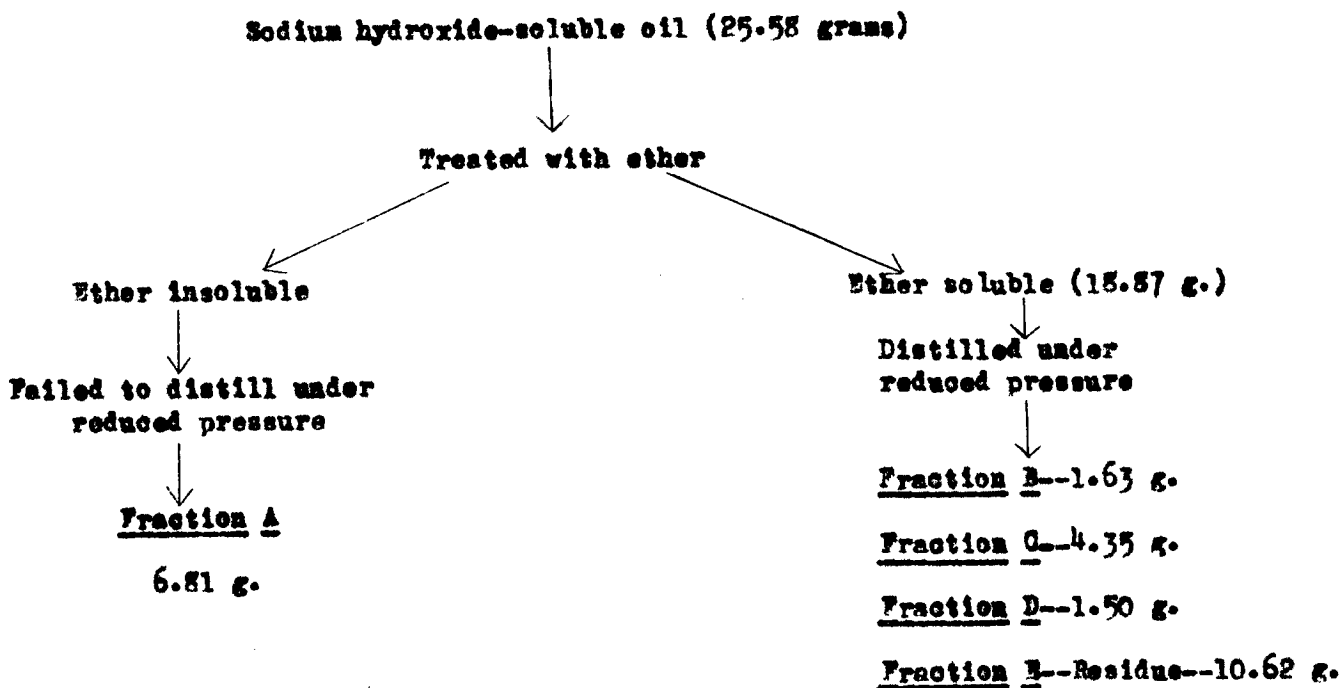


FIGURE 3

Fractionation of Sodium Hydroxide-Soluble Materials

Analysis. Calculated for acetovanillone benzoate,  $C_{16}H_{14}O_4$ :  
C, 71.04%; H, 5.19%. Found: C, 71.12%; H, 5.30%.

In an analogous qualitative large-scale oxidation in which a portion of the oxidised kraft black liquor was lost during the steam distillation of the acidified reaction mixture, a sodium hydroxide-soluble fraction was obtained in the same manner. This fraction distilled at  $150^{\circ} C./0.3-0.7$  mm. The distilled oils were separated physically from the acetovanillone which solidified in the receiving flask. These oils were further fractionated by distillation under reduced pressure. The fractions which were obtained are listed in Table VII.

TABLE VII

FRACTIONS FROM SODIUM HYDROXIDE-SOLUBLE MATERIALS

Fraction	Boiling Point	Characteristic
A	$116^{\circ}/0.17$ mm.	Yellow liquid oil
B	$160^{\circ}/0.24$ mm.	Orange oil
C	$188^{\circ}/0.24$ mm.	Viscous orange oil
D	Residue	Dark tar

A portion from each of the above fractions was treated with each of the following reagents: benzoyl chloride, 3,5-dinitrobenzoyl chloride, p-nitrobenzoyl chloride, and acetic anhydride.

In general, the derivatives obtained were oils. A small amount of a crystalline 3,5-dinitrobenzoate was obtained from Fraction B. After a single recrystallization from ethanol, a tan powder melting at 76-85° C. was obtained. The methoxyl content was 8.31%.

A crystalline benzoate was obtained from Fraction C. After shaking the orange oil with benzoyl chloride and sodium hydroxide, the oily derivative which was formed was extracted with ether. During the extraction, a brown precipitate, which was insoluble in sodium hydroxide or ether, was formed. The precipitate was filtered and recrystallized from dilute dioxane and ethanol. The powdery yellow-brown crystals melted at 173-174° C. and had a methoxyl content of 11.92%.

Analysis. Calculated for  $(C_7H_6O_2)_x$ : C, 68.85%; H, 4.92%.  
Found: C, 68.26%; H, 5.11%.

Assuming one methoxyl group in the molecule, the formula weight calculated from the percentage of methoxyl is 260. This would make the above formula  $(C_7H_6O_2)_2$  or  $C_{14}H_{12}O_4$ , which has a formula weight of 244. Since the above formula permits the substitution of only one benzoyl group, the formula of the original phenolic compound may be  $C_7H_8O_3$  or a multiple of this formula. A search of the literature failed to disclose a phenol  $(C_7H_8O_3$  or  $C_{14}H_{16}O_6)$  with the benzoate melting at 173-174° C. Attention was given to the monomethyl ethers of trihydroxybenzene which have the above formula.

## NITROBENZENE REDUCTION PRODUCTS

### LARGE-SCALE OXIDATION

Extraction of the alkaline reaction mixture from the large-scale oxidation gave 14 liters of a dark amber benzene solution of unreacted nitrobenzene and its reduction products.

A 1400-ml. aliquot (10%) of the above benzene solution was extracted five times with approximately 150-ml. portions of 5% hydrochloric acid to remove aniline. This aniline hydrochloride solution was made alkaline with sodium hydroxide, saturated with sodium chloride, and extracted with ether. The ether extract was dried with anhydrous sodium sulfate, and the ether was removed by distilling in a water bath. Practically pure aniline (58.9 grams) ( $n_D^{20}$  1.554) was obtained.

The benzene extract, after removal of aniline, was distilled under reduced pressure to remove the benzene. The oily residue was fractionated under reduced pressure. The first fraction consisted of 218.4 grams of unreduced nitrobenzene, b.p. 70°/2.4 mm.,  $n_D^{20}$  1.551. The second fraction boiled at 141°/1.2 mm. and solidified into orange crystals which, when recrystallized from ethanol, melted at 67°. A mixed melting point with authentic azobenzene gave no depression. The yield of the azobenzene was 10.1 grams. A small amount of a dark undistillable residue (2.3 grams) was not analysed.

The yields of the above products are summarized in Table VIII. The percentage yield is based on the 3360 grams of nitrobenzene used in the oxidation.

TABLE VIII

NITROBENZENE AND REDUCTION PRODUCTS RECOVERED

	Grams as Nitrobenzene	Yield, %
Nitrobenzene	2184	65.1
Aniline	779	23.2
Azobenzene	137	4.1
Residue	23	0.7
Total	3123	93.1

SMALL-SCALE OXIDATIONS

The ether or benzene solutions obtained by extracting the alkaline reaction mixtures of the small-scale oxidations were not completely analysed, but the presence of nitrobenzene, aniline, azobenzene, and azoxybenzene was indicated. Atmospheric Oxidations 1 and 2 yielded 26.0 and 32.1% aniline, respectively.

In the superatmospheric oxidations, varying amounts of solid material were found in the alkaline reaction mixture. This precipitate was centrifuged or filtered prior to extraction of the nitrobenzene reduction products. Oxidation 5, in which concentrated black liquor was used, was the only oxidation yielding a carbonized residue (20.8 grams) which was insoluble in all solvents. Oxidation 7 gave 2.0 grams of practically pure azobenzene as a precipitate. The remaining superatmospheric oxidations yielded either sodium p-azobenzenesulfonate (SPABS) or a ligninlike precipitate soluble to some extent in water. The amounts of these two materials formed in the various oxidations are summarized in Table IX.

TABLE IX

## PRECIPITATES FORMED IN ALKALINE REACTION MIXTURE

Crude SPABS		Ligninlike precipitate	
Oxidation	Yield. g.	Oxidation	Yield. g.
8	5.0*	6	2.1
9	3.0	12	8.9
10	15.1	14	17.1
11	6.7	15	26.9
13	18.5	16	22.8
19	3.2	17	39.2
21	17.6		

\*Includes 1.2 grams of asobenzene

The SPABS separated from the alkaline reaction mixture as golden platelets which, on recrystallization from ethanol, gave iridescent orange platelets.

Analysis of SPABS Obtained from Oxidation 9. Calculated for  $C_{12}H_9H_2NaO_3S$ : N, 9.86; S, 11.27; Na, 8.10. Found: N, 9.77; S, 10.8; Na, 8.15.

In order to facilitate the identification of SPABS by comparison with authentic SPABS, a benzylthiuronium derivative (13) was prepared in the following manner. To a solution of 1.75 grams of SPABS in 300 ml. of water warmed to 60° C. was added a concentrated aqueous solution of 2.50 grams of benzyl isothiouram hydrochloride with stirring. An immediate precipitate of shiny orange platelets, somewhat lighter in color than the original SPABS, was obtained. After chilling, the derivative was filtered, washed with cold water, air dried, and recrystallized to a constant melting

point from 50% ethanol. The melting point of this new sulfonic acid derivative was 219-220° C. There was no depression of the mixed melting point with the derivative prepared from authentic SPABS (14). A 99.6% yield of the derivative was obtained from authentic SPABS which signifies the quantitative nature of the reaction. Since SPABS has no melting point and, consequently, its purity and yield are difficult to determine, the preparation of the above derivative in practically quantitative yields serves as a rapid method for analysis of SPABS in mixtures free of oxalic acid or other materials which react with the reagent.

Analysis. Calculated for  $C_{20}H_{20}N_4O_3S_2$ : N, 13.08.

Found: N, 13.08.

#### STUDY OF THE FORMATION OF SODIUM *p*-AZOBENZENESULFONATE

Pearl (4) obtained SPABS as a reduction product from the action of sulfite waste liquor and alkali on nitrobenzene only under atmospheric conditions. In a series of experiments, Pearl (14) also proved that the formation of SPABS must result from the reduction of nitrobenzene by lignin in alkaline solution with the subsequent sulfonation of the reduced product in an active state by inorganic sulfites. One of these experiments indicated that an isolated alkali lignin (Meadol) in the presence of inorganic sulfite will reduce nitrobenzene to SPABS. Sodium sulfite alone formed only a small amount of aroxybenzene.

It was previously noted that, in the present study, SPABS was formed only under superatmospheric conditions. A comparison of Oxidations 8 and 15 shows that SPABS is not formed from kraft lignin (Indulin) alone. To

determine whether lignin is responsible for the formation of SPABS when kraft black liquors are used or whether the inorganic constituents of kraft black liquor alone will bring about the formation of SPABS. Oxidation 10 was simulated with a hypothetical black liquor containing only the inorganic constituents. Based on 222 grams water, Table X lists the amounts of salts which were used in addition to the sodium hydroxide and nitrobenzene, using the maximum figures reported by Sutermeister (15).

TABLE X

INORGANIC SALTS USED IN SIMULATED BLACK LIQUOR

	Grams
Sodium carbonate	5.6
Sodium sulfide	4.0
Sodium sulfate	2.7
Sodium thiosulfate	1.4
Sodium sulfite	1.4

The above oxidation produced 17.1 grams of SPABS, which was slightly in excess of that produced by kraft black liquor. To determine which of the above constituents was necessary for the formation of the SPABS, a series of similar oxidations were made, leaving out various constituents. Table XI summarizes the results of these oxidations.

TABLE XI

FORMATION OF SPABS BY INORGANIC CONSTITUENTS

Oxidation	Inorganic Constituents	SPABS, g.
22	NaOH, Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Na <sub>2</sub> SO <sub>3</sub>	17.1
23	NaOH, Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	17.6
24	NaOH, Na <sub>2</sub> S	15.8
25	NaOH, Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Na <sub>2</sub> SO <sub>3</sub>	7.2
26	NaOH, Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>3</sub>	3.3

The above results indicate that the two reducing agents--  
i.e., sodium sulfide and sodium thiosulfate--are mainly responsible for  
the formation of SPABS in the reaction between kraft black liquor and  
nitrobenzene. These reducing agents apparently accomplish a simultaneous  
reduction and sulfonation of the nitrobenzene. The necessity of sodium  
sulfite for the sulfonation was disproved in Oxidation 23. In Oxidation 24  
the sodium sulfide was quantitatively transformed to SPABS.

### ISOLATION OF SODIUM OXALATE

In the small-scale oxidations, varying amounts of sodium oxalate precipitated with SPABS from the alkaline oxidation reaction mixture. An analysis was made of the 18.5 grams of precipitate obtained in Oxidation 13. The alkaline precipitate was dissolved in the minimum quantity of hot water. Ethanol was added to the brown aqueous solution and the gray precipitate was filtered. Additional ethanol was added to the filtrate until a precipitate was no longer obtained. The red filtrate contained the SPABS. The gray precipitate was crystallized from water and dilute ethanol and treated with carbon black to yield 11.3 grams of a white powder. The benzyl isothioureia derivative of this powder melted at 193-194° C. and did not depress a mixed melting point with di-(S-benzylthiuronium) oxalate prepared from authentic sodium oxalate.

Analysis. Calculated for  $\text{Na}_2\text{C}_2\text{O}_4$ : C, 17.91%; Na, 34.33%.

Found: C, 17.91%, Na, 34.07%.

## GENERAL DISCUSSION

In this fundamental study of the reaction between nitrobenzene and kraft black liquor, the first phase involved a determination of the conditions for the optimum yields of lignin degradation products. Previous investigators in the field of lignin oxidation concerned themselves chiefly with obtaining high yields of vanillin. Since guaiacyl compounds other than vanillin have been isolated from lignin and since it was not practicable to make a complete analysis of all the products formed in each small-scale oxidation, it was necessary to obtain a fraction which would contain the various guaiacyl compounds and afford a comparison of the degree of oxidation obtained. Because compounds of the above type are generally soluble in ether or benzene, an extract obtained with the above solvents would represent the degree of oxidation attained. It was later found that benzene extracted a smaller amount of oils and, therefore, all yields were reported as benzene-soluble materials. A typical example of the difference in the amount extracted by ether and benzene is Oxidation 8 in which 66.4% of ether-soluble and only 31.2% of benzene-soluble materials were obtained.

Although a variety of conditions were studied in an attempt to obtain high yields of benzene-soluble materials, the oxidation was not successful from a practical standpoint. The inherent character of the kraft lignin appeared to resist oxidation. This resistance to oxidation may be due to either or both of the following: (1) Substitution of sulfur into the lignin molecule, either as a mercaptan or a sulfide, may inhibit oxidation; (2) the lignin, during the alkaline cooking conditions, is subjected to a reducing action which may alter the lignin molecule and make it less susceptible to oxidation.

Even under drastic conditions, as in the oxidations at 200° C., decomposition of the lignin was difficult. Judging from the smaller amount of precipitated lignin and the darker color of the acidic filtrate obtained in these drastic oxidations, the lignin may have been degraded only into lower molecular weight polymers without yielding lower molecular weight guaiacyl derivatives, or the simple products which may have been formed were recondensed into acid-soluble polymers. These lower molecular weight polymers also composed the greater part of the benzene-soluble fraction of all the oxidations. This is evidenced by the various ligninlike fractions which were isolated from the benzene-soluble materials from the large-scale oxidation.

A similar type of degradation of the lignin may take place under kraft cooking conditions. However, the products in the two cases are not necessarily the same but both may be formed as a result of alkaline hydrolysis. Extraction of the acidified unoxidized kraft black liquor yielded 28.9% of benzene-soluble materials. The nature of these materials was not investigated. The methoxyl content of 10.08% demonstrated that they originated principally from the lignin. The benzene-soluble materials represented a recovery of 20.5% of the methoxyl in the black liquor. Hagglund (17) found acetovanillone in kraft black liquor in an amount of about 0.1% of the wood weight, which is further evidence that kraft lignin is severely degraded under alkaline cooking conditions.

The determination of the nature of the ether-soluble extract obtained from the alkaline black liquor was not within the original scope of this work. Since both liquid and solid materials with a mercaptan odor

(actually identical with the kraft odor) were obtained, there is a possibility that these materials also originated from the lignin. Further investigation of these materials may lead to a better understanding of the chemistry of the kraft process. Removal of these substances by a more practical means may also solve the kraft odor problem. After a long period, the ether-extracted black liquor regained the original kraft odor to a lesser degree, which indicates that these odoriferous substances can be formed by internal reaction or decomposition.

Nitrobenzene oxidation of the kraft black liquor also destroys the mercaptan odor. In general, the oxidation reaction mixtures had an ammonia or nitrobenzene odor. After the ether or benzene extraction of the nitrobenzene products, the extracted reaction mixture retained only the odor of the solvent. After evaporation of the solvent no odor remained. Since mercaptan materials were not found in the extract of the nitrobenzene reduction products, the mercaptans were probably completely oxidized.

The benzene-soluble products were also devoid of a mercaptan odor. However, the benzene-soluble materials after the crystalline sulfur was removed gave a qualitative sulfur test. This indicates that sulfur may have been chemically combined with the lignin fragments which were extracted with benzene. A negative nitrogen test indicated that there was no condensation between the nitrobenzene products and the benzene-soluble lignin degradation products. An examination of the sulfur-containing oil which sublimed with the vanillic acid from the bisulfite-soluble materials failed to disclose the nature of the chemical combination of the sulfur in the oil.

The presence of inorganic sulfur compounds in the black liquor had far-reaching effects on the oxidation. The study of the variables of the reaction showed that a much higher ratio of nitrobenzene was required in this study than was required for the oxidation of sulfite waste liquor (1, 4). This was due to the reducing action of the inorganic salts--chiefly sodium sulfide and sodium thiosulfate--which were present in the black liquor. The effect of these salts on nitrobenzene was forcibly demonstrated in the study made on the formation of sodium p-nitrobenzenesulfonate. It is believed that the oxidation of these salts preceded or, at any rate, was accomplished with less difficulty than the oxidation of the lignin. However, their presence in the reaction mixture had no deleterious or retarding effect on the oxidation of the lignin if a large excess of nitrobenzene was used. This was demonstrated by the fact that the yield of benzene-soluble materials was not increased by substituting an alkaline solution of Indulin for the black liquor. On the contrary, the appreciable decrease in yield from Indulin (compare Oxidations 8 and 15) leads to the belief that materials other than lignin in the black liquor may exert a beneficial catalysing action on the oxidation. Inasmuch as only one oxidation was made on Indulin, the above cannot be stated as a definite conclusion. The fact that the methoxyl content of the benzene-soluble fractions from the Indulin oxidation was in the same range (less than the methoxyl content of lignin) as that of the black liquor oxidations dispels the belief that the benzene-soluble materials from the black liquor oxidations contained a large proportion of black liquor extractives such as fats, waxes, and resins. The presence of substances with a low methoxyl content in the benzene-soluble fraction may be accounted for by the fact that demethylation of the products

may have occurred. This loss of methoxyl was not apparent in the methoxyl balance for the large-scale oxidation.

Although nitrobenzene is classified as a mild oxidizing agent, the combined effect of high temperature and the presence of alkali may result in extreme degradative action, as indicated above. Additional signs of degradation were observed in the case of the small-scale oxidations made at 200° C. These oxidations yielded a ligninlike precipitate in the alkaline reaction mixture. Bergström, Cederqvist, and Trobeck (16) found that, by heating kraft black liquor to 325-350° C. under pressure, a large amount of the organic matter in the liquor was precipitated as a carbonaceous mass. However, the above-noted precipitates in the present study were not carbonaceous. The precipitate obtained in Oxidation 13 was composed mainly of sodium oxalate. The large yield which was obtained indicated that either the lignin or, more probably, the lignin oxidation fragments were severely degraded, or a degradation of the sugar acids present in black liquor occurred. Presumably both took place, but the former may account for the accompanying low yields of benzene-soluble materials in these drastic oxidations. Although the precipitates from the other oxidations were not analysed, their appearance and solubility in water lead to the belief that they also contained a large proportion of sodium oxalate. A smaller amount of sodium oxalate was probably formed in the less drastic oxidations. Although no attempt was made to determine the nature of the liquid products, the presence of acetic acid and formic acid was suspected.

In addition to the variables which were studied, it was found that the degree of oxidation is also a function of the amount of agitation

during the oxidation. This was demonstrated by the much lower yield of benzene-soluble materials obtained in the large-scale oxidation. The yield in the large-scale oxidation was 17.6%, whereas a yield of 31.2% was obtained in Oxidation 5. The only difference between the two oxidations, apart from the quantity used, was the type of autoclave (more satisfactory types were not available) used and, consequently, the degree of agitation. This also partially accounts for the extremely low yields of crystalline oxidation products isolated from the large-scale oxidation. The atmospheric oxidations were made with rapid stirring, but failed to give high yields of benzene-soluble materials. However, it is believed that the yields could be greatly increased by more rapid agitation and/or a longer reaction time.

The two main crystalline products obtained from the oxidation of lignin were vanillic acid and acetovanillone. The combined yield of vanillic acid from the bicarbonate- and bisulfite-soluble fractions was 25.33 grams (7.93 and 17.40 grams, respectively) or 1.78% based on the lignin. The yield of acetovanillone from the sodium hydroxide-soluble fraction of the benzene-soluble materials was 9.41 grams or 0.66% based on the lignin. Vanillin was isolated from an analogous large-scale oxidation which, because of the loss of a portion of the reaction products, was carried out qualitatively. This vanillin was isolated in an unconventional manner since it was obtained from the acidified bisulfite solution from which the bisulfite-soluble materials were supposedly extracted with ether. Evidently the vanillin was not liberated because of the evolution of sulfur dioxide being continually generated from the decomposition of some product in the boiling acid solution. The vanillin was finally isolated by distilling the acidified bisulfite solution to dryness and extracting the residue with ethanol. That vanillin

is a product of the oxidation of kraft black liquor was also indicated in a small-scale oxidation made under the same conditions as Oxidation 1. In this case, an aliquot of the bisulfite extract was treated as above for the removal of the sulfur dioxide. The vanillin was then precipitated as the 2,4-dinitrophenylhydrazone. From the weight of the derivative, which had a methoxyl content of 8.50% (theoretical methoxyl--9.34%), the yield of vanillin from this oxidation was calculated to be 6.4%. This value for vanillin may be high as it may include some acetovanillone which is also soluble in bisulfite solution and also forms a 2,4-dinitrophenylhydrazone under the conditions employed.

In an attempt to develop a rapid method for the determination of the vanillin, the potentiometric titration method of Siggia and Maxcy (19) was examined on a known weight of authentic vanillin. The titration gave no break in the plotted curve and, hence, no end point was indicated. This may have been due to the reversibility of the reaction to form vanillin and sodium bisulfite as additional amounts of sodium hydroxide were added during the titration.

The bisulfite-soluble fraction from the quantitative large-scale oxidation yielded vanillic acid instead of the vanillin which was expected. This may be attributed to any of several causes. It is possible that some vanillic acid may have been extracted by the bisulfite solution, or the vanillin, which is readily susceptible to oxidation, may have been oxidized to vanillic acid during the sublimation treatment. Another explanation, which is based on the extremely long time required for the complete sublimation of the vanillic acid from the oily bisulfite-soluble extract, is that the

vanillic acid was the result of decomposition of a low molecular weight polymer of lignin. The actual possibility of the latter was investigated by a cursory analysis of the sulfur-containing oil which sublimed with the vanillic acid. The nature of this compound was not definitely established because of the low yield.

An additional amount of vanillic acid was isolated from the bicarbonate-soluble fraction using the procedure developed by Pearl (16) which is based on the solubility in aqueous solution of the lead salt of vanillic acid. Since a large portion of the bicarbonate-soluble fraction was insoluble in water, the technique was further extended to afford a fractional separation of the remaining water-insoluble materials by dissolving and precipitating the lead salts from a dilute ethanol solution. In this manner five fractions were obtained from the bicarbonate-soluble materials. Crystalline materials were obtained from all the fractions except one. With the exception of vanillic acid, these crystalline materials were not completely identified because of their small yields. Fraction C, which embraced the compounds whose lead salts were soluble in dilute ethanol and remained in solution after the alcohol was distilled, yielded a white crystalline compound on sublimation which had the empirical formula  $C_9H_9O_2$  and melted at 129-130° C. Analysis, which was incomplete, indicated that this compound resembled, in some respects, the structures of cinnamic acid and coumarin. Three additional crystalline compounds were isolated from the various fractions of the bicarbonate-soluble materials. Extreme difficulty was encountered in the purification of these compounds. This fact, coupled with the small yields, made it possible to report only the method of isolation and the crude melting points. A further

investigation of the structure of the above compounds isolated in larger amounts may be of aid in the understanding of the chemistry of lignin.

The sodium hydroxide-soluble materials were fractionated according to their solubility in ether. The ether-soluble materials were further separated into more distinct fractions by distillation under reduced pressure. Although these phenolic materials had a definite guaiacol odor, acetovanillone (whose yield was reported above) was the only compound definitely identified. The other phenolic materials were oils which did not boil under reduced pressure at any definite temperature. Also, crystalline derivatives could not be obtained from these oils, with the exception of two compounds. One yielded a small amount of a tan powdery 3,5-dinitrobenzoate which melted at 76-85° C. and had a methoxyl content of 8.31%. The other was a yellow-brown powdery benzoate which melted at 173-174° C. and had a methoxyl content of 11.92%. This benzoate had the empirical formula  $C_7H_6O_2$ . The assembled data demonstrated that the original phenolic compound may have the empirical formula  $C_7H_8O_3$ . An insufficient amount of the derivative was available to prove this by saponification and further analysis.

The nature of the nitrobenzene reduction products and the study of the formation of sodium *p*-azobenzenesulfonate are discussed in the preceding separate section.

### SUMMARY AND CONCLUSIONS

In this study of the oxidation of kraft black liquor with nitrobenzene, the optimum yield of benzene-soluble products was 31.2% based on the lignin.

A somewhat similar oxidation made on a larger scale to permit the separation and identification of the above cleavage products gave a yield of 17.6%. Vanillic acid accounted for 10.1% (yield of 1.78% based on lignin) and acetovanillone for 3.8% (0.66% based on lignin) of the fraction. Vanillin and oxalic acid were also isolated and identified. In a similar large-scale oxidation, the yield of vanillin was approximately 0.3% (based on lignin), in contrast to the yield of 6.4% (based on lignin) which was obtained in a small-scale oxidation.

A procedure, which was based on the solubilities of the lead salts in water and dilute ethanol, was developed for the fractionation of the bicarbonate-soluble materials into five separate divisions. Crystalline compounds were isolated from four of these fractions by means of sublimation. The data obtained on one of these compounds indicates some similarity of this compound ( $C_9H_9O_2$ ) to cinnamic acid and coumarin.

Two unidentified phenolic derivatives were prepared from compounds present in the sodium hydroxide-soluble fraction. The remainder and greater portion of the benzene-soluble materials consisted of oils and amorphous materials which represented either higher molecular weight lignin cleavage products or condensation products of the lignin.

The nitrobenzene reduction products formed in the large-scale oxidation consisted of aniline and azobenzene. In addition to these, azoxybenzene and sodium p-azobenzenesulfonate (SPABS) were formed in some of the small-scale oxidations. A procedure was established for the quantitative determination of SPABS in the form of its benzyl iso-thiuronium salt.

A study of the formation of SPABS indicated that sodium sulfide and sodium thiosulfate were chiefly responsible for the formation of SPABS in the reaction between kraft black liquor and nitrobenzene. These reducing agents accomplished a simultaneous reduction and sulfonation of the nitrobenzene.

In connection with the study of the nature of the extractable materials of kraft black liquor, an odorless black liquor was obtained by ether extraction of the odoriferous materials. These materials, which had a mercaptan odor, were separated into solid and liquid fractions. A 28.9% yield (based on lignin) of benzene-soluble materials was obtained from the above black liquor after acidification. This represents a recovery of 20.5% of the methoxyl in the black liquor and indicates that lignin is severely degraded under kraft pulping conditions.

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