beyond the seal to make contact with mercury in the side tube, which could be lengthened and bent in any convenient way. All work was done in an ordinary blast lamp using gas and air. The foil adheres firmly to the large tube and forms an electrode which is definitely fixed. No difficulty was found when the platinum black was deposited and the cell with two such electrodes was used repeatedly at temperatures between 0 and 115° without change in constant. The lead-in seal was definitely gas tight. Although a cell of this kind might be rather difficult to make with electrodes of large area, this difficulty is readily avoided since the modern vacuum tube amplifier renders large electrodes unnecessary. The total weight of the electrode in this case was only about four milligrams, a point not without interest where cost is concerned.

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THE CHEMISTRY OF LIGNIN. III. THE DESTRUCTIVE DISTILLATION OF LIGNIN FROM CORN COBS

BY MAX PHILLIPS

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During the past few years a number of papers have appeared on the destructive distillation of lignin. All of the work thus far published has been confined to the lignin isolated from wood. Heuser and Skiöldebrand[1] destructively distilled lignin isolated from spruce sawdust by the method of Willstätter and Zechmeister.[2] Their results calculated on the ash-free lignin were as follows: carbon residue, 50.64%; oil, 13.00%; acetone, 0.19%; methanol, 0.90%; acetic acid, 1.09%.

Hägglund[3] distilled lignin isolated from pine wood by the hydrochloric acid method of Willstätter and Zechmeister and obtained 45% carbon residue, 9.6% oil, 0.10% acetone, 0.67% methanol and 0.64% acetic acid.

Fischer and Schrader[4] distilled Willstätter lignin and obtained 13.2% aqueous distillate, 12.5% oil, 57.2% carbon residue and 17.0% gas (obtained by difference). It was found that 16.4% of the oil dissolved in sodium carbonate and 33.9% in sodium hydroxide solution.

[2] Canadian Pulp and Paper Association Research Fellow.

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[1] Heuser and Skiöldebrand, *Z. angew. Chem.*, I, **32**, 41 (1919).

[2] Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

[3] Hägglund, *Arkiv. för Kemi, Min. och Geol.*, **7**, 1 (1918); *Chem. Zentr.*, **90**, III, 186 (1919).

[4] Fischer and Schrader, *Abhand. Kohle*, **5**, 106 (1920).

Tropsch[5] destructively distilled commercial Willstätter lignin under reduced pressure (1–2 mm.) and obtained 14.2% aqueous distillate, 10.2% oil and 53.8% carbon residue. The oil contained 37.5% phenolic compounds.

Pictet and Gaulis[6] distilled under reduced pressure commercial Willstätter lignin isolated from fir. They obtained 15% oil, 21% aqueous distillate and 52% carbon residue. No examination of the aqueous distillate was made. The oil was extracted with 10% sodium hydroxide, in which 89% dissolved. In the alkali-soluble fraction eugenol was identified. The alkali-insoluble fraction was separated by means of liquid sulfur dioxide into saturated and unsaturated hydrocarbons. In the fraction containing the saturated hydrocarbons melene was identified.

The present paper contains results on the destructive distillation of lignin from corn cobs. The lignin used in the destructive distillation experiments was prepared by three different methods: the alkali method, the fuming hydrochloric acid method of Willstätter and the 72% sulfuric acid method. The results obtained tend to support the claim that the lignin fraction obtained from corn cobs by the alkali method is quite different in composition from that obtained by either the Willstätter or the 72% sulfuric acid method. While some differences in the results were noted also in the lignin prepared by the two last mentioned methods, the principal difference was between the alkali lignin on the one hand and the Willstätter and 72% sulfuric acid lignins on the other.

The results recorded in the literature on the destructive distillation of lignin are limited entirely to lignin isolated from wood by the Willstätter method, and in comparing those results with that recorded in this paper on the lignin isolated from corn cobs by the same method, it is observed that the values, with exception of that recorded for the yield of acetone, are of the same general order of magnitude. The yield of acetone was much higher in the case of lignin isolated from corn cobs than that recorded in the literature on lignin from wood (compare Tables I and II). Whether this may be attributed to an essential difference in the composition of the lignins from the two sources, or is due to some impurity present, it is difficult to state, considering our present fragmentary knowledge of the chemistry of lignin.

Experimental

Preparation of Lignin by the Alkali Method.—The corn cobs were treated with six times their weight of 2% sodium hydroxide solution and heated in an autoclave for eight hours under 25 pounds' pressure. The alkaline liquors were then drained off, the cobs were washed with a stream of water and the wash water was added to the alkaline liquor. This liquor was filtered and then made acid with an excess of either 50% sulfuric

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[5] Tropsch, *Abhand. Kohle*, **6**, 293 (1921).

[6] Pictet and Gaulis, *Helv. Chim. Acta*, **6**, 627 (1923).

acid or with concentrated hydrochloric acid. This was heated to boiling and boiled for half an hour, allowed to cool to room temperature, then centrifuged in a basket centrifuge and finally dried at 100°. The yield amounted to from 4 to 5% of the weight of the cobs taken. The lignin thus obtained was free from cellulose and when distilled with 12% HCl, according to the Official A. O. A. C. Method,[7] gave a precipitate with phloroglucinol corresponding to 2.45% pentosans as calculated by the Kröber formula.

A methoxyl determination was made according to the Kirpal and Bühn[8] modification of the Zeisel[9] method. The iodine was, however, determined gravimetrically as silver iodide instead of volumetrically as recommended by Kirpal and Bühn.

Anal. Subs., 0.4682, 0.6678 (calcd. on ash-free basis): AgI, 0.5075, 0.7223. Found: OCH_3, 14.31, 14.28.

Preparation of Lignin by the Fuming Hydrochloric Acid Method.—The procedure recommended by Willstätter and Kalb[10] was followed, except that a longer period was allowed for the hydrochloric acid to act upon the corn cobs. Corn cobs (200 g.) ground to pass through a 20-mesh sieve were mixed with four liters of fuming hydrochloric acid (d = 1.21 at 15°) and allowed to stand at room temperature for twenty-four hours. The flask containing the reaction mixture was shaken from time to time. To the reaction mixture 1300 g. of crushed ice was added and it was allowed to stand for another twenty-four hours. It was then diluted further with six liters of water, filtered on a Büchner funnel using a woolen filter cloth in place of filter paper, and washed with water until the wash water no longer gave a test for the chlorine ion with silver nitrate. The product, which was almost black in color, was dried at 100°; yield, 23.5–25% calculated on the weight of the cobs used. It contained 1.05% of ash.

A methoxyl determination made on this material gave the following results: Subs., 0.3088, 0.3236 (calcd. on ash-free basis): AgI, 0.1988, 0.2123. Found: OCH_3, 8.50, 8.66.

Preparation of Lignin by the 72% Sulfuric Acid Method.—Corn cobs, ground to pass through a 20-mesh sieve were mixed with four liters of 72% sulfuric acid and allowed to stand at room temperature for thirty-six hours. The reaction mixture was shaken from time to time. At the end of the thirty-six hour period a sample of the reaction product was examined microscopically in parallel polarized light with crossed nicols and was found to be free from doubly refractive substances.[11] The reaction product was diluted with four times its volume of water, heated to boiling and maintained at this temperature for one hour. The product was filtered off and washed with hot water until free from sulfuric acid. It was dried at 100°. The yield amounted to 19% of the weight of the cobs. It contained 1.10% of ash.

A methoxyl determination made on this material gave the following results. Subs., 0.3083, 0.3111 (calcd. on ash-free basis): AgI, 0.2242, 0.2253. Found: OCH_3, 9.61, 9.57.

Apparatus Used.—The destructive distillation experiments were conducted in a copper retort which was heated in a bath consisting of a eutectic mixture of sodium–potassium nitrate. The retort was connected to a weighed distilling flask which served as a

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[7] "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Washington, D. C., **1925**, p. 120.

[8] Kirpal and Bühn, *Ber.*, **47**, 1084 (1914); *Monatsh.*, **36**, 853 (1915).

[9] Houben, "Die Methoden der Organischen Chemie," Georg Thieme, Leipzig, **1923**, Vol. III, p. 144.

[10] Willstätter and Kalb, *Ber.*, **55**, 2640 (1922).

[11] The microscopic examinations were made by Mr. George L. Kennan of the Microchemical Laboratory of the Food, Drug and Insecticide Administration.

condenser and receiver. The distilling flask was cooled with water and connected in series to another receiver which was cooled with ice.

Experimental Procedure and Analysis.—In each experiment 50 g. of lignin was used. After several preliminary tests it was determined that 380–400° was the optimum temperature for carrying out the destructive distillations, which usually required about four hours to complete. The distillate was collected in a weighed receiver and its weight determined. The result thus obtained is recorded in Table I, under the heading "Total Distillate." The oily portion was separated mechanically from the aqueous distillate and weighed, and the weight of the aqueous distillate obtained by difference. The amount of gaseous substances produced was obtained by deducting the combined weight of "Total Distillate" and non-volatile carbon residue left in the retort from the weight of the original lignin.

The aqueous distillate was purified with activated charcoal (Darco) as recommended by Stritar and Zeidler,[12] filtered into a 200- or 250-cc. volumetric flask and made up to the mark. The percentage of methanol in this solution was determined by the method of Stritar and Zeidler.[12] The acetone was determined by the Messinger[13] method, which was carried out as follows: twenty cc. of the solution to be analyzed was measured into a 300-cc. glass-stoppered Erlenmeyer flask. To this was added 20 cc. of *N* sodium hydroxide solution and an excess (about 50%) of *N*/10 iodine solution. This was well shaken, allowed to stand for one hour and 20.3 cc. of *N* hydrochloric acid added; the excess of iodine was determined by titration against *N*/10 sodium thiosulfate solution.

The organic acids in the aqueous distillate were determined either by titration against *N*/10 sodium hydroxide solution or, when the color of the solution did not permit direct titration, by boiling an aliquot of the aqueous distillate with an excess of barium carbonate for about one hour under the reflux condenser, filtering off the unused barium carbonate and determining the barium in the filtrate gravimetrically as barium sulfate. In either case the results were calculated as acetic acid. The results obtained are recorded in Table I.

It will be observed from Table I that the results are quite different in the case of alkali lignin than that of the lignin isolated by either the Willstätter or 72% sulfuric acid method. The yields of aqueous distillate and oil were much higher, whereas the yields of carbon residues were lower in the experiments with alkali lignin than with lignin prepared by the other two methods. In this connection it may also be stated that the carbon residues from alkali lignin were light and spongy, whereas those from the other two preparations were generally obtained either in the form of hard lumps or as a black powder.

As regards the composition of the aqueous distillate, it will be observed from Table I that a higher methanol yield but lower acetone and acetic acid yields were obtained from alkali lignin than from Willstätter and 72% sulfuric acid lignin. The higher methanol yield from alkali lignin is undoubtedly due to its higher methoxyl content. The low yield of acetic acid obtained from alkali lignin may be explained by the fact that in preparing lignin by this method deacetylation occurs. This has been shown by Pringsheim and Magnus[14] and confirmed repeatedly in this

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[12] Stritar and Zeidler, *Z. anal. Chem.*, **43**, 387 (1904).

[13] Messinger, *Ber.*, **21**, 3366 (1888).

[14] Pringsheim and Magnus, *Z. physiol. Chem.*, **105**, 179 (1919).

TABLE I

RESULTS ON DESTRUCTIVE DISTILLATION OF LIGNIN FROM CORN COBS

In experiments marked "A"—alkali lignin was used. In experiments marked "B"—Willstätter lignin was used. In experiments marked "C"—lignin isolated by 72% H_2SO_4 method was used.

Expt. no.	Lignin Quantity used (grams)	Lignin Ash-free lignin (grams)	Total distillate Grams	Total distillate Calcd. on ash-free lignin %	Aqueous distillate Grams	Aqueous distillate Calcd. on ash-free lignin %	Oil Grams	Oil Calcd. on ash-free lignin %
1-A	50	49.1	16.58	33.7	7.51	15.2	9.07	18.5
2-A	50	49.1	16.10	32.7	7.61	15.5	8.49	17.3
3-A	50	49.1	16.28	33.1	7.55	15.4	8.73	17.8
4-A	50	49.1	16.34	33.2	7.86	16.0	8.48	17.2
5-B	50	49.48	12.90	26.0	8.90	17.9	4.0	8.0
6-B	50	49.48	9.60	19.4	6.10	12.3	3.5	7.0
7-C	50	49.45	10.48	21.2	7.51	15.1	2.97	6.0
8-C	50	49.45	12.19	24.6	7.37	14.9	4.8	9.7

Expt. no.	Carbon residue Grams	Carbon residue Calcd. on lignin used %	Gas (by difference) Grams	Gas (by difference) Calcd. on ash-free lignin, %	Components of aqueous distillate: Acetone Grams	Acetone Calcd. on ash-free lignin, %	Methanol Grams	Methanol Calcd. on ash-free lignin, %	Acid Calcd. as acetic acid, grams	Acid Calcd. on ash-free lignin, %
1-A	26.2	52.4	6.3	12.8	0.0408	0.08	0.9692	1.97	0.0247	0.05
2-A	26.2	52.4	6.8	13.8	.0630	.12	.9642	1.96	.0264	.05
3-A	26.0	52.0	6.8	13.8	.0750	.15	.8959	1.82	.0336	.06
4-A	26.0	52.0	6.8	13.8	.0878	.17	.8963	1.82	.0250	.05
5-B	29.5	59.0	7.6	15.3	.3000	.60	.3480	0.70	.5702	1.15
6-B	29.0	58.0	11.4	23.0	.2718	.54	.3466	.70	.5160	1.04
7-C	31.5	63.0	8.02	16.2	.4420	.89	.4280	.86	.4700	0.95
8-C	34.0	68.0	3.81	7.7	.5877	1.18	.5950	1.2	.4348	.87

Laboratory. The writer has always obtained negative results when making acetyl determinations by the Perkin[15] method upon alkali lignin isolated from corn cobs.

The yields of acetone obtained from alkali lignin are of the same general order of magnitude as that reported on Willstätter lignin from wood by Heuser and Skiöldebrand[1] and by Hägglund.[3] However, the acetone yields from the lignin prepared from cobs by the Willstätter and by the 72% sulfuric acid methods were much higher than those recorded in the literature.

For purpose of comparison, the data reported in the literature on the destructive distillation of lignin are recorded in Table II.

The oil obtained in the four distillation experiments with alkali lignin (24.6 g.) was dissolved in ether and successively extracted with 5% sodium bicarbonate solution and 5% potassium hydroxide solution. The ether solution which had thus been extracted was dried over anhydrous calcium chloride, the ether was removed by evaporation and the residue was weighed. The result thus obtained is recorded in Table III under "Hydrocarbons and Inert Compounds." The potassium hydroxide and so-

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[15] Perkin, *Proc. Chem. Soc.*, **20**, 171 (1904).

TABLE II

RESULTS ON DESTRUCTIVE DISTILLATION OF LIGNIN REPORTED BY VARIOUS INVESTIGATORS

Investigators	Source of lignin	Method used for isolating the lignin	Carbon residue %	Oil %	Aqueous distillate %	Gas (by difference) %	Acetone %	Methanol %	Acetic acid %
Heuser and Skiöldebrand	Spruce	Fuming HCl method of Willstätter	50.64	13.0	..	..	0.19	0.90	1.09
Hägglund	Pine	Fuming HCl method of Willstätter	45.0	9.6	..	..	0.10	0.67	0.64
Fischer and Schrader	Coniferous wood	Fuming HCl method of Willstätter	57.2	12.5	13.2	17.0	..	..	..
Tropsch	....	Fuming HCl method of Willstätter	53.8	10.2	14.2	..	..	..	..
Pictet and Gaulis	Fir	Terrise and Levy Patent (essentially the Willstätter method)	52.0	15.0	21.0	..	..	..	..

dium bicarbonate extracts were acidified and extracted with ether. The ether solutions were dried over anhydrous sodium sulfate, the ether was distilled off and residues weighed. The results obtained are given in Table III.

TABLE III

ANALYSIS OF OIL

	Percentage of oil by weight
Acids	8.6
Phenols	84.0
Hydrocarbons and neutral compounds	7.2

The phenolic portion of the oil was repeatedly fractionated. After several fractionations it was resolved into three fractions: 204–208°, 208–225° and 225–240°. Fraction 204–208° gave an orange color with ferric chloride solution. A picrate prepared according to the directions given in Mulliken, Vol. 1, page 91, melted at 85°. This fraction, therefore, consisted principally of guaiacol. It amounted to 2.3% of the weight of lignin distilled. Fraction 208–225° was not identified. Fraction 225–240° gave a greenish-blue coloration with ferric chloride solution. An alcoholic solution of it gave a blue color with ferric chloride. A benzoyl derivative prepared from this fraction melted at 70.5°. This fraction, therefore, contained eugenol.

Summary

Lignin prepared from corn cobs by the alkali method, the fuming hydrochloric acid method of Willstätter and by the 72% sulfuric acid method, was subjected to destructive distillation under ordinary atmospheric pressure and at a temperature of 380 to 400°. From the alkali lignin the following results, representing the average of four experiments (calculated on the basis of ash-free, dry lignin) were obtained: aqueous distillate, 15.5%; water-insoluble oily distillate, 17.7%; carbon residue

(calculated on the quantity of lignin used), 52.2%; gas, 13.5% (by difference); acetone, 0.13%; methanol, 1.9%; water-soluble acids (calculated as acetic acid), 0.05%. The oily distillate analyzed as follows: (The results are expressed as per cent. by weight of the oil) acids, 8.6%; phenols (fraction soluble in 5% KOH solution and insoluble in 5% $NaHCO_3$ solution), 84.0%, hydrocarbons and neutral compounds, 7.2%. In the phenolic portion of the oil guaiacol and eugenol were identified.

In the case of the Willstätter lignin and the lignin prepared by the 72% sulfuric acid method, the percentage of aqueous distillate was about the same as that obtained from alkali lignin, whereas the oily distillate was only about one-half. The percentages of carbon residues obtained from the Willstätter lignin and from the 72% sulfuric acid lignin were considerably greater than that obtained from alkali lignin. The percentages of acetone and acetic acid obtained were considerably greater in the case of the Willstätter and the 72% sulfuric acid lignin than in the alkali lignin, whereas, the percentage of methanol was less. This higher percentage of methanol is probably due, in part, to the greater methoxyl content of alkali lignin than that of Willstätter and 72% sulfuric acid lignin. A possible explanation for the lower yield of acetic acid obtained from alkali lignin is presented.

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NEW CONDENSATIONS OF KETONES WITH PHENOLS. III. CONDENSATION PRODUCTS OF MESITYL OXIDE AND MONOHYDROXYBENZENES

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Introduction

In continuation of the studies of the condensation possibilities of ketones with phenols, as begun with the condensation system phorone–cresols,[2] the condensation systems of mesityl oxide with monohydroxybenzenes were investigated. The discussion of the results of these investigations is the purpose of this communication.

Theoretical Part

By treating a molar mixture of mesityl oxide and a monohydroxybenzene with concentrated sulfuric acid in the cold, condensation products are ob-

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[1] In collaboration with Nathan Ambinder, Richard Casty, De Witt C. Knowles, Irving Rappaport and William Saschek.

[2] Niederl, THIS JOURNAL, **50**, 2230 (1928); Niederl and Casty, *Monatsh.*, **51**, 1028 (1929).