products by the action of ethanolic hydrogen chloride, the extent of the reconversion decreasing with increasing complexity of the lignin fraction.

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[Contribution from the Division of Industrial and Cellulose Chemistry, McGill University]

Studies on Lignin and Related Compounds. LVII. Mechanism of the Ethanolysis Reaction

By William B. Hewson, Joseph L. McCarthy and Harold Hibbert

By treating maple wood with ethanol–hydrogen chloride, 30% of the lignin (Klason) can be isolated as water-soluble "distillable oils" (containing "lignin building units" of the propylphenol type[1]) while the remainder of the lignin either is isolated as a water-insoluble amorphous material, or else remains in the wood. In the present investigation an attempt was made to remove *all* of the lignin from wood in the form of "distillable oils" or, failing this, to ascertain the factors interfering with such an accomplishment.

Accordingly, maple woodmeal was treated, under various conditions, with ethanol and hydrogen chloride, the ethanol reaction mixture separated, and the woodmeal residue examined for unremoved lignin. The ethanol solution was neutralized, concentrated and poured into water, and the insoluble lignin removed. Concentration of the aqueous solution brought about separation of the "lignin tar," while benzene extraction of the aqueous solution yielded the water-soluble lignin or crude "distillable oils."

An attempt (Table I) was first made to decrease the proportion of residual lignin (Klason), amounting to about 30% when forty-mesh maple woodmeal was used,[2] by increasing the surface area of the wood by grinding in a ball mill. This effected only a slight improvement in lignin removal and no marked change in yield of "distillable oils" (Expts. 9–11). Results with maple wood in the form of "Asplund" fiber, produced by disk grinding[3] of maple chips (in which the middle lamella lignin[4] should be freely accessible to the extractant), gave a similar negative result (Expt. 12). A slightly higher yield of "distillable oils" was obtained in one case (Expt. 13) in which a somewhat larger solvent-to-wood ratio was used, a factor known to bring about this effect.[5] In Expt. 15, using ordinary woodmeal (40 mesh), the ethanolysis was carried out with simultaneous grinding in a ball mill and using a higher acid concentration to compensate for the lower temperature conditions. The yield of "distillable oils" was much lower. No change was found in the ethanolysis of younger wood, for example one year old maple woodmeal (Expt. 14). Factors other than the physical nature of the wood thus appear to be operative in controlling the delignification and yield of "distillable oils."

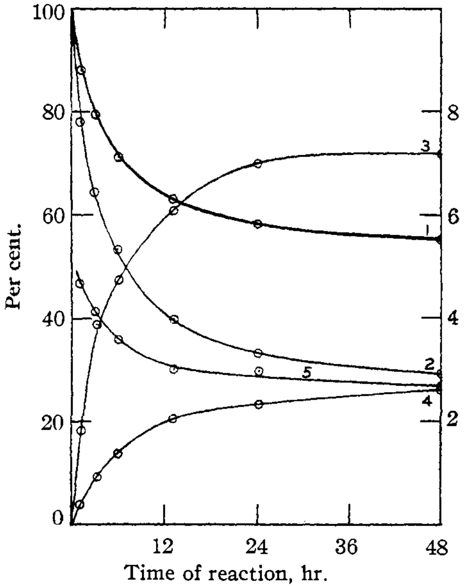

Fig. 1.—(1) Yield of residual wood; (2) original lignin in residual wood; (3) original lignin isolated as ethanol lignin and "lignin tar"; (4) original lignin isolated as "distillable oils"; (5) ratio of (ethanol lignin + "lignin tar")/"distillable oils," scale on right.

In Expts. 1–6, Fig. 1, the ethanolysis reaction was carried out for varying periods of time (1–48 hr.). The residual lignin (Curve 2) decreased progressively to a final constant value, equal to about

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[1] See review by Hibbert, *Paper Trade J.*, **113**, no. 4, 35 (1941).

[2] Brickman, Pyle, McCarthy and Hibbert, This Journal, **61**, 868 (1939).

[3] Asplund, U. S. Patent 2,008,892, July 23 (1935).

[4] Bailey, *Ind. Eng. Chem., Anal. Ed.*, **8**, 52 (1936).

[5] K. A. West, Hawkins and Hibbert, unpublished results.

TABLE I

EFFECT OF REACTION CONDITIONS ON YIELDS OF MAPLE WOOD PRODUCTS FROM THE ETHANOLYSIS REACTION AT 78°

Expt.	Sample	HCl concn., %		Time, hr.	Residual wood, %		Lignin balance,[b] %					Ratio R
		Initial	*Final*[a]		*Yield*	Klason Lignin	Lignin in residual wood	Ethanol lignin	"Lignin tar"	"Distillable Oils"	Total accounted for	
1	Woodmeal	2	1.7	1	88.3	19.3	78.7	14.0	4.7	4.0	101.4	4.7
2	Woodmeal	2	1.5	3	79.1	17.9	65.0	33.0	6.4	9.6	114.0	4.1
3	Woodmeal	2	1.4	6	71.4	16.5	53.9	39.5	8.1	13.2	114.7	3.6
4	Woodmeal	2	1.2	13	63.3	14.2	40.0	52.5	9.0	20.8	122.3	3.0
5	Woodmeal	2	1.0	24	58.8	12.4	33.6	60.0	10.4	23.4	127.4	3.0
6	Woodmeal	2	0.7	48	55.9	11.6	29.4	66.0	6.2	26.3	127.9	2.7
7	Residual woodmeal	2	...	48	46.8	10.4	22.2[c]	7.0[c]	0.9[c]	2.1[c]	...	..
8	Ethanol lignin	2	...	60	..	..	20.4[d]	57.4	6.6	5.4	89.8	12.1
9	Wood flour	2	1.4	6	58.7	15.1	43.1	48.9	4.6	17.1	113.7	3.1
10	Wood flour	2	1.2	12	43.5	13.4	27.9	66.9	6.2	23.1	124.1	3.2
11	Wood flour	2	0.7	48	34.8	11.6	19.6	77.8	2.1	26.8	126.3	3.0
12	"Asplund" fibers	2	1.4	6	69.5	17.0	57.8	38.1	4.4	14.1	114.4	3.0
13	"Asplund" fibers	2	0.7	48	51.6	11.1	28.0	62.4	8.1	34.8	133.3	2.0
14	Young wood	2	.7	48	48.5	21.4	48.0	59.0	3.6	21.1	131.7	3.0
15	Woodmeal[e,g]	5	...	90	84	19	65.9	22.4	6.8	4.8	99.9	6.1
16	Woodmeal	2[f]	2[f]	100	43.4	9.9	23.5	73.1	5.9	20.0	122.5	4.0
17	Woodmeal	0.5[f]	0.5[f]	100	51.0	11.2	31.1	61.5	5.6	16.9	115.1	4.0
18	Woodmeal	6	...	48	50.4	13.8	32.3	86.5	4.0	21.8	144.6	4.1
19	Woodmeal[h]	20	8.0	150	57.5	13.9	37.0	65.9	5.4	20.7	129.0	3.4

[a] Concentration of hydrogen chloride found by titration of an aliquot portion of the reaction mixture. [b] The percentages are given on the basis of the weight of lignin (Klason) in the starting material. Since an alkoxyl group has been added to most of the lignin products, the percentages are subject to correction by a factor of $L/(L + (OC_2H_5))$, where L equals the molecular weight of the lignin units. [c] Calculated on the basis of the lignin (Klason) in the wood prior to the two ethanolysis treatments. [d] Represents a cold ethanol-insoluble lignin. [e] Carried out in a ball mill. [f] Acid concentration maintained constant throughout the reaction. [g] Temp. 25–30°. [h] Temp. 0–50°.

30% of the original lignin, while the "distillable oils" (Curve 4) increased to about 26%, the final values being reached in forty-eight hours. Since a gradual decrease in the acid concentration occurred during the reaction period, the residual woodmeal was re-treated with fresh original extractant (Expt. 7). Only a slight further removal of lignin took place, presumably indicating that the residual lignin is structurally different from the solubilized portion. Re-treatment of a precipitated ethanol lignin with ethanol–hydrogen chloride (Expt. 8) converted about 20% into a new type of lignin (A), insoluble in cold and difficultly soluble in hot ethanol and probably related to the "residual lignin" left after the customary ethanolysis. Comparison of this isolated insoluble lignin (A) (OCH_3, 22.5%[6]; reduced viscosity, 770[7]) with the alcohol-soluble ethanol lignin (B) (OCH_3, 24.5%[6]; reduced viscosity, 480[7]) indicated a considerably greater degree of molecular complexity in the former.

In Table II are shown the results obtained with a woodmeal sample after successive brief treatments with ethanol–hydrogen chloride, followed in each case by successive removals of the extraction liquor and replacement with *fresh* reagent, thus shortening time of contact of reaction products with the extractant. In this way 93% of the original lignin was removed in alcohol-soluble form as compared with about 65% under the usual conditions.[2] The low yield of residual pulp (29%) indicated that considerable hydrolysis of carbohydrates had occurred. Probably secondary reactions undergone by these materials gave rise to the abnormal increase in residual lignin observed after the repeated twenty-four hour treatments (Table II, Series IV, Column 7). Since this complete delignification might have been caused by the maintenance of a constant acid concentration (2%) during this prolonged reaction period, another ethanolysis was carried out (Table I, Expt. 16) in which sufficient hydrogen chloride was added intermittently during the reaction period to maintain the concentration as close to 2% as possible, and for a time period equal to the total time of reaction in the "re-treatment" ex-

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(6) Total alkoxyl calculated as methoxyl.

(7) Patterson, West, Lovell, Hawkins and Hibbert, THIS JOURNAL, **63**, 2065 (1941).

TABLE II

EFFECT OF A SHORT SERIES OF SUCCESSIVE RE-TREATMENTS ON THE YIELD OF MAPLE WOOD ETHANOLYSIS PRODUCTS

Successive Re-treatments[a]				Residual wood, %		Lignin balance,[b] %					
Series	No.	Time of each hr.	Total time, hr.	Yield	Klason lignin	Lignin in residual wood	Ethanol lignin	"Lignin tar"	"Distillable oils"	Total accounted for	Ratio, *R*
I	4	1	4	65	15.4	46.5	42.7	12.6	11.6	113.3	4.8
II	3	4	16	53	9.3	22.6	17.7	2.7	5.2	115.1[c]	3.9
III	3	9	43	23	6.7	7.1	8.6	2.2	2.4	112.8[c]	4.5
	2	11	65								
	1	24	89								
IV	9	24	305	29	5.9	8.0	1.6	..	..	115.3[c]	
Total	22		305	*final lignin balance*		8.0	70.6	17.5	19.2	115.3[c]	4.6

[a] Carried out at 78° with an HCl concentration of 2%. [b] See footnote (b), Table I. [c] Totals obtained by using the percentages of ethanol lignin, "lignin tar," and "distillable oils" from Groups I, II, or III where necessary.

periment (Table II). The amount of original lignin left in the wood residue (23.5%) in this non-intermittent treatment (Expt. 16) indicated that the intermittent removal of the ethanolic liquors (Table II) evidently decreased the extent of the condensation–polymerization, thus facilitating delignification.

The yield of "distillable oils" obtained in the "re-treatment" experiments (Table II) was considerably lower than usual, indicating that short contact with the ethanol–hydrogen chloride (Expt. 6) was an important factor in regard to yield of "distillable oils." Consideration of the ratio

$$R = \frac{\text{ethanol lignin} + \text{``lignin tar''}}{\text{``distillable oils''}},\ i.e.\ \frac{\text{ethanol-soluble water-insoluble products}}{\text{water-soluble products}}$$

shows that, as the ethanolysis reaction proceeds, the value of *R* decreases progressively (Expts. 1–6), indicating a greater proportion of water-soluble lignin present in solution as compared with the water-insoluble type. If the "distillable oils" were present, as such, in the wood, they should be readily extractable and, if readily polymerizable, would produce an opposite trend (an increase) in the value of *R* over that actually found. Since such is not the case, as also shown in the following communication, presumably they are formed actually by the cleavage of protolignin or its simple polymers at reflux ethanolysis temperature, especially since a low yield of "distillable oils" is associated with the high value of *R* obtained at room temperature in the ball mill (Expt. 15). This theory finds further support in the formation of "distillable oils" when an isolated ethanol lignin is subjected to ethanolysis (Expt. 8).

The delignification process, as well as that of the formation of water-soluble "distillable oils," possibly takes place as a result of hydrolysis of a lignin polymer or a lignin carbohydrate complex, in view of the well-known[8] hydrolytic characteristics of a solution of hydrogen chloride in alcohol. The actual solubilizing of the wood constituents by the ethanolic reaction mixture is probably facilitated both by the increased solubility of the etherified[1] lignin products and also by use of a finely-divided wood so that effects due to physical factors of penetration, etc., are minimized. Polymerization and condensation reactions accompanying ethanolysis give rise to insoluble forms of lignin which exert an important role in connection with its removability. Thus the basis of the ethanolysis mechanism is to be found in simultaneously progressive *depolymerization* and *polymerization* changes, the degree to which these proceed being influenced by the conditions of the reaction. The limitation in attainable yields of "distillable oils" would seem to be based on fundamental differences in the reactivity of the constituent groups present in the side chains of the propyl phenol (C_6–C_3) lignin building units, either already isolated, or related to other assumed plant respiratory catalysts, from which protolignin is derived.[1] Recent hydrogenation studies of isolated lignin materials[9] have indicated that these units are capable of polymerization to give condensation polymers of both a C—O—C and C—C—C type. Presumably the former readily undergo fission by acids to yield the simpler molecules, while the latter would be inert to reagents such as ethanol–hydrogen chloride. It seems possible that in maple protolignin the

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(8) Voss and Wachs, *Ann.*, **522**, 240 (1936).

(9) Cooke, McCarthy and Hibbert, THIS JOURNAL, **63**, 3056 (1941).

C—O—C type predominates and is present in the form both of relatively simple molecular aggregates and of more complex units. Under the influence of the extractant (ethanol–hydrogen chloride) both depolymerization and polymerization changes may occur, with the formation of the simple molecular "distillable oils" on the one hand and non-reversible polymers on the other.

Experimental

Preparation of Starting Materials.—Air-dried **maple woodmeal** (40 mesh) was extracted forty-eight hours with anhydrous ethanol-benzene (1:1), followed by twenty-four hours with anhydrous ethanol, then washed with hot water for twelve hours, air and vacuum dried. The final product contained 3% water and 21.6% lignin (Klason).[10] **Maple wood flour** was prepared from woodmeal by dry grinding for forty-eight hours in a ball mill. **"Asplund" maple wood fibers,** prepared on the Asplund defibering machine, were screened to remove coarse material, and extracted as above; lignin content, 21.6%. Woodmeal was prepared from maple wood about one year old by removing the bark from twigs which had been allowed to stand eight months in ethanol, then grinding to a fine meal and extracting as above. **Residual maple woodmeal,** remaining after ethanolysis[2] of woodmeal from older wood, contained 12.8% lignin. **Maple ethanol lignin**[2] was freed from water-soluble components by twice precipitating from ethanol into water (1:10).

Ethanolysis Procedures.—In general, following the previous method,[2] the prepared starting material (equivalent to 100 g. of dry weight) was refluxed in an inert atmosphere (carbon dioxide) with anhydrous ethanol (800 cc.) containing hydrogen chloride (variable quantities). In the different experiments varying amounts of starting material were sometimes employed but the ratio of woodmeal to ethanol was always maintained at 100 g. to 800 cc., with one exception (Expt. 13) in which a ratio of 100 g. to 1600 cc. was used. After a given time (variable) the reaction mixture was filtered, the **residual woodmeal** washed with ethanol (200 cc)., weighed and analyzed for its lignin content. The combined ethanol filtrate and washings were neutralized (sodium bicarbonate), filtered to remove inorganic salts, concentrated (150 cc.) in an inert atmosphere (carbon dioxide) at reduced pressure, and precipitated into water (1000 cc.). The precipitated **ethanol lignin** was washed with cold water, dried under vacuum and weighed. The aqueous filtrate and washings were concentrated (250 cc.) in an inert atmosphere (carbon dioxide) at reduced pressure whereupon a reddish **"lignin tar"** (not previously reported) separated. This was washed with water, dried under vacuum and weighed. The concentrated aqueous solution was continuously extracted with benzene, the latter removed and the residual, dried, water-soluble **"distillable oils"** then weighed.

In one case (Expt. 15) the reaction was carried out using 5% hydrogen chloride for ninety hours with simultaneous grinding in a ball mill at 25–30°. In the series of treatments in which the acid concentration was maintained constant (Expts. 16 and 17) at each of fifteen appropriate periods during the 100-hour refluxing, an aliquot of the reaction mixture was removed, titrated with standard alkali to determine the concentration of hydrogen chloride, and then sufficient additional ethanol–hydrogen chloride (30% solution) added to maintain the desired concentration. Using an initial concentration of 20% hydrogen chloride in ethanol (Expt. 19), the woodmeal was stirred for twenty-five hours at 0°, ten hours at 20°, seventy-five hours at 25° and forty hours at 45–50°.

In the "re-treatment" experiment (Table II) woodmeal (100 g. "bone dry" weight) was refluxed for one hour with anhydrous ethanol (800 cc.) containing dry hydrogen chloride (2%), after which the reaction mixture was filtered, washed with hot ethanol (100 cc.) and dried under suction on a Büchner funnel covered with a thin rubber sheet. The residual wood was then treated for three similar one-hour periods with fresh portions (800 cc.) of ethanol containing hydrogen chloride (2%), with subsequent filtration, washing and drying after each period. The combined ethanol liquors from these four treatments were neutralized with an alcoholic solution of sodium ethylate, filtered to remove sodium chloride, concentrated, precipitated into water and examined as in the ethanolysis procedure described above. An aliquot of the residual wood left after the lignin extraction was removed and analyzed for moisture and lignin content so that a complete lignin balance could be calculated at this stage of the re-treatment. The remaining residual wood was then treated in a similar manner for three four-hour periods and the lignin balance at this second stage determined as above. The third stage consisted of similar treatments for longer periods. Maximum delignification was attained, since further treatment of the residue for nine additional twenty-four-hour periods with ethanol (400 cc.) containing hydrogen chloride (2%) extracted only a small amount of lignin-like material.

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Summary

1. An extensive investigation of the effects produced by varying the conditions (time, acid concentration and physical nature of the wood) employed in the ethanolysis of maple wood resulted in no additional increase in the yield of lignin "distillable oils."

2. By the use of a modified ethanolysis extraction process, it was possible to remove practically the entire lignin content of the wood. This was accomplished by the stepwise removal and replacement of the ethanol–hydrogen chloride medium used as extractant, in this way minimizing the tendency of the lignin to undergo condensation–polymerization reactions.

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[10] Ritter, Seborg and Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

3. The mechanism of ethanolysis is shown to involve both depolymerization and polymerization reactions. Low molecular weight lignin "distillable oils" are formed by cleavage of high molecular lignin aggregates, while simultaneous polymerization reactions yield a complex, non-reversible, ethanol-insoluble lignin polymer, the formation of which limits both the attainable yield of "distillable oils" and the degree of delignification.

MONTREAL, CANADA RECEIVED JULY 21, 1941

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LVIII. The Mechanism of the Ethanolysis of Maple Wood at High Temperatures

BY WILLIAM B. HEWSON, JOSEPH L. McCARTHY AND HAROLD HIBBERT

In the preceding paper[1] evidence was presented indicating that during the course of ethanolysis at 78°[2] the larger part of maple wood protolignin is progressively removed and simultaneously converted, or degraded, into a mixture of ethanol-soluble "distillable oils" and amorphous ethanol lignin, and to a smaller extent is polymerized or condensed into ethanol-insoluble lignins which remain in the woody residue. Since only the former types of products are readily recoverable in a form suitable for further study,[2] an investigation has been made of the mechanism of ethanolysis and the effectiveness of ethanol, in the presence of various catalysts, in bringing about removal of the lignin from maple wood at higher than reflux temperatures.

While only small amounts of "native lignin" are extracted from wood (spruce) by treatment with ethanol at room temperature,[3] recent work[4] indicates that extensive delignification of aspen wood occurs on treatment with aqueous butanol (1:1) at a high temperature (158°). To correlate this effect with that of ethanol, carefully dried maple wood was treated for various periods with anhydrous ethanol at 150, 165, 180 and 200°, respectively, and the yield of residual wood and the lignin content (Klason)[5] determined (Expts. 1–13). As shown in Table I, only about 10% of the protolignin is removed by prolonged treatment at 150° with ethanol alone, whereas more than 60% is dissolved at 78° in the presence of ethanol and hydrogen chloride (2%).[1] This limited delignification (at a temperature where penetration and diffusion should proceed without hindrance) must be due to the fact that the lignin units (ethanol-soluble in the isolated state[2]) either do not exist in wood in simple monomolecular form or are combined with each other and probably also with carbohydrates as ethanol-insoluble aggregates.

The removal of lignin and perhaps also the breakdown of a portion into "distillable oils" by ethanolysis is apparently brought about largely by the cleavage or hydrolytic influence[6] of the hydrogen chloride present in the alcohol reagent. In the experiments starting with pure ethanol, acidic substances were found present in small amounts even during the treatment at 150° since after nine hours the *p*H of the solution was 4.5, while after seven hours at 200° the *p*H had decreased to 4.3. Acids, such as formic and acetic, are formed by the action of water on wood at temperatures up to 200°[7] and they have been found to accelerate greatly the delignification of straw with ethylene glycol.[8] These probably function as catalysts in the above experiments with anhydrous ethanol, their influence on the rate of delignification becoming more marked as the reaction temperature is increased. When either hydrogen chloride or sodium hydroxide is added to the ethanol extraction medium, the rates of delignification at elevated temperatures are very rapid (Expts. 14–25, Table I), indicating that concentration of hydrogen or hydroxyl ions is an important factor.

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[1] Hewson, McCarthy and Hibbert, THIS JOURNAL, **63**, 3041 (1941).

[2] (a) Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939); (b) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); (c) Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939); (d) Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940); (e) Brickman, Pyle, Hawkins and Hibbert, *ibid.*, **62**, 986 (1940).

[3] (a) Klason, *Ber.*, **65**, 625 (1932); (b) Klason, "Beiträge zur chemischer Zusammensetzung des Fichtenholzes," Gebrüder Borntraeger, Berlin, 1911; (c) Brauns, THIS JOURNAL, **61**, 2120 (1939).

[4] (a) Bailey, *Paper Trade J.*, **110**, no. 1, 29 (1940); (b) Bailey, *ibid.*, **110**, no. 2, 29 (1940).

[5] Ritter, Seborg and Mitchell, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 202 (1932).

[6] Voss and Wachs, *Ann.*, **522**, 240 (1936).

[7] (a) Aronovsky and Gortner, *Ind. Eng. Chem.*, **27**, 451 (1935); (b) Corey and Maass, *Can. J. Research*, **13B**, 289 (1935).

[8] Erbring, *Papierfabr.*, **37**, Tech. Tl., 168 (1939).