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 simultaneously poly- merization 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.

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 pH of the solution was 4.5, while after seven hours at 200° the pH 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.

(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).

If this is the case, addition of water to an alcoholic reaction medium, for example, bu-

TABLE I

LIGNIN EXTRACTION FROM MAPLE WOOD BY ETHANOLYSIS UNDER VARIOUS CONDITIONS

Expt. no.	Extractant Ethanol (%)	Water (%)	Catalyst Type	Amount (%)	Temp., °C.	Time, hr.	Yield, %	Residual woodmeal Lignin content, %	Per cent. of original lignin remaining
1	100	none	none	...	150	1.5	99.0	21.2	97.1
2	100	none	none	...	150	5	96.0	20.4	90.5
3	100	none	none	...	150	9	96.0	20.0	88.8
4	100	none	none	...	165	1	98.0	19.8	89.8
5	100	none	none	...	165	4	94.0	19.3	83.7
6	100	none	none	...	165	10	89.5	18.0	74.7
7	100	none	none	...	180	1	96.0	19.5	86.5
8	100	none	none	...	180	4	90.5	17.5	73.5
9	100	none	none	...	180	10	85.5	15.7	62.0
10	100	none	none	...	200	2	83.0	17.2	65.3
11	100	none	none	...	200	7	76.0	12.8	45.0
12	100	none	none	...	200	16.5	72.0	10.6	35.3
13	100	none	none	...	200	36	68.0	10.2	31.9
14	100	none	HCl	0.1	165	1	68.7	8.9	28.3
15	100	none	HCl	0.1	165	4	61.5	6.0	17.1
16	100	none	HCl	0.1	165	10	55.1	5.0	12.8
17	100	none	HCl	0.1	180	1	57.0	6.3	16.5
18	100	none	HCl	0.1	180	5	51.0	4.1	13.4
19	100	none	HCl	0.1	180	9	49.0	4.5	10.1
20	100	none	NaOH	2.0	140	1	60.4	7.4	16.2
21	100	none	NaOH	2.0	140	1.5	53.2	3.7	9.0
22	100	none	NaOH	2.0	140	4	41.6	1.2	2.3
23	100	none	NaOH	2.0	165	1	38.6	4.0	7.1
24	100	none	NaOH	2.0	165	4	24.0	0	0
25	100	none	NaOH	2.0	165	10	20.8	0	0
26	50	50	none	...	165	1	87.5	17.8	72.0
27	50	50	none	...	165	4	57.3	9.3	24.6
28	50	50	none	...	165	10	55.1	5.5	14.0
29	50	50	HCl	0.1	120	1.5	70.8	15.0	49.1
30	50	50	HCl	0.1	120	3	61.5	11.1	31.6
31	50	50	HCl	0.1	120	6	50.0	7.1	16.4
32	50	50	HCl	0.1	140	1	53.1	7.8	19.2
33	50	50	HCl	0.1	140	2.5	46.0	3.7	7.9
34	50	50	HCl	0.1	140	4.5	45.0	3.3	6.9
35	50	50	HCl	0.1	165	1	44.8	2.1	4.4
36	50	50	HCl	0.1	165	4	36.5	2.8	4.7
37	50	50	HCl	0.1	165	10	26.1	21.9	26.4
38	50	50	HCl	1.0	165	0.33	44.7	3.1	6.5
39	50	50	HCl	1.0	165	0.66	39.6	2.8	5.1
40	50	50	HCl	1.0	165	1	35.4	5.4	8.9
41	50	50	NaOH	2.0	120	0.5	84.4	20.1	78.5
42	50	50	NaOH	2.0	120	1.5	73.0	16.7	56.2
43	50	50	NaOH	2.0	120	6	69.0	10.1	32.2
44	50	50	NaOH	2.0	140	1	67.8	11.0	34.5
45	50	50	NaOH	2.0	140	2.5	62.5	5.5	15.9
46	50	50	NaOH	2.0	140	4.5	58.5	2.7	7.4
47	50	50	NaOH	2.0	165	1	58.4	2.3	6.2
48	50	50	NaOH	2.0	165	4	54.0	0.5	1.2
49	50	50	NaOH	2.0	165	10	46.9	0	0
50	none	100	none	...	165	1	72.0	25.5	76.5
51	none	100	none	...	165	4	69.0	30.2	96.0
52	none	100	none	...	165	10	67.0	32.7	101.0
53	none	100	NaOH	2.0	165	1	59.5	12.4	34.1
54	none	100	NaOH	2.0	165	4	53.1	4.8	11.8
55	none	100	NaOH	2.0	165	8	49.0	1.8	4.1

TABLE II

YIELDS OF LIGNIN PRODUCTS OBTAINED FROM MAPLE WOOD BY HIGH TEMPERATURE EXTRACTION METHODS

	Reaction conditions					Residual woodmeal, %		Lignin balance,[a] %					
	Extractant, %		Catalyst		Temp.,	Time,		Lignin con-	Lignin in resid- ual	Eth- anol	"Lig- nin	"Dis- till- able	Total ac- counted	Ratio,
Expt.	Ethanol	Water	Type	Amount, %	°C.	hr.	Yield	tent	wood	lignin	tar"	oils"	for	R[b]
56	100	None	None	...	200	4	75.2	15.2	52.7	33.6	11.5	7.1	104.9	6.4
57	100	None	HCl	0.1	200	2	52.0	5.3	12.7	76.5	7.7	17.9	114.8	4.7
58	100	None	NaOH	2.0	165	2	39.4	2.5	4.6	89.7	9.0	13.5[e]	116.8	7.3
59	50	50	HCl	0.1	165	2	47.7	4.1	15.6	82.7	14.5	19.7	132.5	4.9
60[d]	50	50	NaOH	2.0	165	2	55.8	1.3	3.5	59.5	15.2	21.6	99.8	3.5

[a] The percentages are given on the basis of the weight of lignin (Klason) in the starting material. The large percentages of material accounted for are probably due in some cases to alkylation of the lignin as in the case of acid extractions, and to complex condensation reactions as in the case of the alkaline extractions.   [b] $R = \dfrac{\text{ethanol lignin} + \text{"lignin tar"}}{\text{"distillable oils"}}$

[e] Methoxyl content, 20.6% (calculated as total alkoxyl).   [d] Results obtained by John R. Bower, Jr.

tanol,[9] whereby ionization of the catalyst is increased, should bring about a more rapid cleavage and delignification and this was found to be the case. In the present investigation, the same accelerating effect was found with wood treated at 165° with an equal mixture of ethanol and water, but no catalyst (Expts. 26–28, Table I). After ten hours only about 14% of the original lignin remained undissolved in contrast to about 75% using anhydrous ethanol under the same conditions (Expt. 6). Likewise when acidic or alkaline catalysts are added to the ethanol–water extraction medium (Expts. 29–49, Table I), the rate of delignification is accelerated and to a greater degree as the concentration of catalyst increases. Although Bailey[4] attempted to buffer his butanol–water mixture at pH 7 in order to show that delignification can proceed under neutral conditions, his evidence cannot be regarded as established because the effectiveness of buffers at elevated temperatures has never been proved, as pointed out recently by Corey and Maass.[10]

With a relatively high concentration of hydrogen ions in an ethanol–water reaction mixture (Expts. 35–40), delignification is rapid at first but as the reaction proceeds the relative percentage of a more insoluble lignin in the residual wood increases due to condensation-polymerization changes. This more insoluble type of lignin is probably similar to that formed on ethanolysis of an isolated ethanol lignin.[1] Such changes apparently proceed to a considerable extent even in the presence of water alone (Expts. 50–52). With sodium hydroxide as catalyst, the redeposition of lignin was not observed (Expts. 41–49 and 53–55), presumably due to alkali solubility

of the lignin product. Viewed from the lack of success experienced by Adkins, Frank and Bloom[11] in isolating simple molecular products from the reaction mixture obtained by hydrogenation of alkali lignin, it seems probable that the lignin undergoes partial polymerization or condensation in the presence of alkali at high temperature.

Nevertheless, a small amount of protolignin is converted to "distillable oils" even when the ethanolysis reaction, using various alcoholic media, is carried out at high temperatures (165 and 200°) (Table II). The yields of "distillable oils," although not as high as at a lower temperature (78°), are nevertheless significant, especially since they are obtained under conditions involving a practically complete removal of the lignin. These reaction products are now being investigated.

The interpretations of the course of the wood ethanolysis reactions in this and the preceding[1] paper are in general harmony with Hägglund's views[12] relating to sulfite pulp manufacture. Both recognize the important influence of hydrogen and hydroxyl ions in accelerating the cleavage of linkages between lignin–lignin and lignin–carbohydrate units as well as the necessity of establishing conditions such that the hydrolyzed lignin is actually soluble in the reaction mixture.

Experimental

Preparation of Starting Materials.—Air-dried maple woodmeal (40 mesh) was extracted forty-eight hours with anhydrous ethanol–benzene (1:1), followed by anhydrous ethanol for twenty-four hours. It was washed with hot water for twelve hours, air- and vacuum-dried; moisture content 3%; lignin (Klason)[5] 21.6%. It was subjected to an additional drying, in some cases, by treatment with several successive portions of dry ethanol.[13]

(9) (a) Aronovsky, U. S. Patent 2,037,001, April 14, 1936; (b) Aronovsky and Gortner, *Ind. Eng. Chem.*, **28**, 1270 (1936).

(10) Reference 7[b], footnote p. 295.

(11) Adkins, Frank and Bloom, THIS JOURNAL, **63**, 549 (1941).

(12) (a) Hägglund, *Papierfabr.*, **24**, Tech. Tl., 449 (1925); (b) Hägglund, *ibid.*, **27**, 165 (1929).

(13) Kennedy and Rulon, U. S. Patent 2,102,799, Dec. 21 (1938).

Lignin Extraction Experiments (Table I).—Maple wood-meal (9.6 g.) (moisture-free whenever used in anhydrous ethanol medium) was placed in a stainless steel pressure vessel (250 cc.) along with the extraction medium (180 cc.). The vessel was securely closed, then immersed in an oil-bath at a temperature so regulated that the immersion of the cold vessel lowered the temperature to the desired reaction temperature. After an appropriate time interval, the vessel was removed, cooled by immersion in cold water, opened, and the residual wood filtered from the reaction liquors and washed with ethanol. When sodium hydroxide was used as catalyst, the wood residue was washed thoroughly with hot water and then with ethanol. In all experiments the wood residue was finally extracted with ethanol in a Soxhlet extractor, air-dried, weighed and analyzed.

In Expts. 3 and 11, after filtration of the ethanol reaction liquor, the pH was measured.

Investigation of Lignin Reaction Products (Table II).—Dry woodmeal (40 g.) (3% moisture content) and anhydrous ethanol (400 cc.) were placed in a stainless steel pressure vessel (500 cc.) equipped with an inside Monel metal baffle to aid stirring. The vessel was fitted into a steel frame in which it was rotated (250 r. p. m.) throughout the experiment, the entire apparatus being immersed in an oil-bath, the temperature of which was accurately controlled. After a suitable reaction period the assembly was removed from the oil-bath, the vessel disengaged and cooled in water. In general the reaction products were examined by the method previously described.[1]

After filtering the reaction mixture, the insoluble **residual woodmeal** was extracted continuously with ethanol (in the case of alkali extractants (Expts. 58, 60), it was then washed with hot water (1000 cc.)) and, after vacuum drying, analyzed for lignin. The ethanol filtrate and extraction liquors were combined, neutralized (sodium bicarbonate), concentrated (100 cc.) under reduced pressure in a nitrogen atmosphere and precipitated into water (1000 cc.). The **ethanol lignin** precipitate was washed with cold water (50 cc.), dried under reduced pressure, and weighed. The aqueous filtrate and washings were concentrated under reduced pressure in a nitrogen atmosphere. The reddish "lignin tar" which separated was washed with water, vacuum-dried and weighed. The concentrated aqueous solution was extracted continuously with benzene from which the water-soluble "distillable oils" were isolated. In addition to the ethanol lignin, "lignin tar" and "distillable oils" obtained from the ethanol liquors, further amounts of these products were obtained from the aqueous washings necessary when sodium hydroxide was present (Expts. 58 and 60). These were neutralized (dilute hydrochloric acid), and the resulting **alkali ethanol lignin** filtered off, dried at reduced pressure and weighed. The aqueous filtrate was concentrated and extracted with benzene as before, whereupon "lignin tar" and "distillable oils" products were obtained. In Table II, showing these results, the two sets of yields of amorphous lignin, "lignin tar" and "distillable oils" are combined in the one value reported.

Summary

1. The high temperature delignification of maple wood using ethanol, either alone or in the presence of various catalysts (water, hydrogen chloride, and sodium hydroxide), has been investigated.

2. Removal of only about 10% of the protolignin from dry maple wood by treatment at 150° with anhydrous ethanol indicates that the p-propylphenol type building units do not exist in wood in the monomolecular form but are in combination with other units, or with carbohydrates, or with both, as ethanol insoluble aggregates.

3. Delignification of maple wood by ethanolysis involves cleavage of linkages between lignin–lignin or lignin–carbohydrate units or both and is catalyzed by the presence of hydrogen or hydroxyl ions in the reaction mixture. Increase in temperature accelerates the cleavage and removal of the lignin is facilitated by the presence of an appropriate solvent.

4. Significant amounts of lignin "distillable oils" of low molecular weight are formed by ethanolysis of maple wood at high temperatures either in the presence or absence of acids or of alkalies.