

DESTRUCTIVE DISTILLATION of LIGNOCELLULOSE

► ► ► Compounds with different cellulose and lignin contents, as produced by a wood hydrolysis process, were carbonized to determine the source of the various products. By varying the ratio of lignin and cellulose, a better understanding of the mechanism of distillation may be attained and applied to the treatment of naturally occurring lignocellulose.

Various lignocellulose compounds, pure cotton cellulose, soluble lignin, and maple wood were destructively distilled in a retort. From the data obtained the following conclusions were drawn: Acetic acid is derived principally from the cellulose while methanol is obtained solely from the lignin. Hemicellulose in wood is the chief source of acetic acid. Soluble lignin forms larger yields of charcoal and noncondensable gases and a lower yield of total aqueous distillate than does cotton cellulose. The various lignocellulose compounds give larger yields of tar than either cotton cellulose or soluble lignin.

MANY investigators have destructively distilled the natural hard- and softwoods, cellulose, lignin, bagasse, corneobs, and other agricultural waste materials, but none has destructively distilled other than natural lignocellulose compounds. The purpose of this work was to observe and compare the products obtained by carbonizing specially prepared compounds containing "soluble" lignin, "insoluble" lignin, and cellulose in various known and controlled ratios, so as to understand better the mechanism of distillation of naturally occurring lignocellulose.

The reaction of carbonization is exothermic at about 275° C., and the exothermic heat amounts to about 6 per cent of the heat of combustion of wood. Water and carbon dioxide gas (3) are first evolved (endothermic stage), followed by the release of illuminants, methane, and aliphatic compounds (exothermic stage); and finally the charcoal and polymerized products (tar) are further broken down to secure larger yields of by-products (third stage). It has been stated (3) that cellulose yields very little methanol but considerable acetic acid, whereas lignin in general gives greater percentages of methanol and acetic acid (from the acetyl or methoxyl groups present). The yields of these products are therefore largely dependent upon the relative proportions in which cellulose and lignin are present. Hurd (2) states that pentosans give acetic acid and considerable furfural, besides the usual gas and tar by-products. Kurth and Ritter (5) also believe that carbohydrates are the source of acetic acid.

Jacobs (3) found that resins from the interaction of furfural and phenol are often present. Crude pyroligneous liquors almost invariably contain small percentages of nitrogen compounds, and frequently nitrogen occurs in the noncondensable gases.

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The formula of cellulose is $(C_6H_{10}O_5)_x$; the formula proposed for lignin from maple wood (1) is $C_{42}H_{30}O_8(OCH_3)_6(OH)_4$, with two ethylenic double bonds and a minimum molecular weight of 910.

Material Used

SOURCE. The lignocellulose compounds were supplied by the Northwood Chemical Company which uses a continuous dilute sulfuric acid hydrolysis to produce lignocellulose residues for plastics. In a typical continuous hydrolysis run (4) one pound of maple wood flour (24 mesh) is suspended in 10 pounds of water containing 0.3 pound of sulfuric acid. This suspension is then pumped at a rate of 0.5 gallon per minute (2-minute hydrolysis at 300 pounds per square inch) through a steam-heated double-pipe heat exchanger; the temperature of the suspension leaving the tube by an automatic valve ranges from 170° to 180° C. A yield of approximately 56 per cent lignocellulose residue results. The residue is filtered, washed, dried, and ground.

ANALYSIS. For the isolation of soluble lignin, the dry hydrolyzed substance obtained from the hydrolysis process is extracted in a Soxhlet apparatus with methanol. The methanol extract is poured into several times its own volume of water. The soluble lignin which precipitates is filtered, washed, and dried. The lignin which is not extracted with methanol is called "insoluble" lignin.

The insoluble lignin is determined by treating the dry extracted material with 72 per cent sulfuric acid at 20° C. for 2 hours. This mixture is diluted to a 3 per cent solution and refluxed for 4 hours to convert the cellulose to sugars. The residue is the insoluble lignin. Subtracting the percentage of soluble and of insoluble lignin from 100 gives the percentage of cellulose remaining unhydrolyzed after the original process. Small amounts of hemicellulose thus are included, although most of this fraction is hydrolyzed in the early stages of the process.

The percentage compositions of the lignocellulose compounds used follow:

Compound No.	15/29	316	345	333
Soluble lignin	15%	15	9	33
Insoluble lignin	20%	36	43	29
Total lignin	44%	51	52	62
Cellulose	56%	49	48	38

Carbonization Procedure

RETORT. The retort (Figures 1 and 2) was built of a 4-inch standard steel pipe with a flange screwed on each end. Two end plates were made of 1/4-inch steel and drilled with mating bolt holes for 5/8-inch bolts. Gaskets of 1/4-inch sheet asbestos were made for each end and were impregnated with a graphite-water paste before use. A 1 1/2-inch steel pipe vapor neck, 6 1/2 inches long and threaded at its upper end, was welded on at the midpoint.

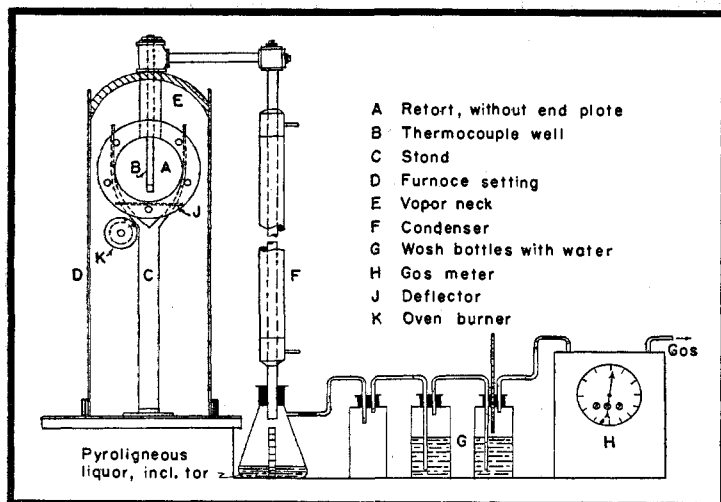


Figure 1. Diagram of Apparatus, Showing End Cross Section of Furnace Housing

A $1\frac{1}{2} \times 1\frac{1}{2} \times \frac{3}{4}$ inch tee was joined to the vapor neck; its $\frac{3}{4}$ -inch branch was connected to a $\frac{3}{4}$ -inch cross by a $\frac{3}{4}$ -inch horizontal iron pipe, $9\frac{1}{2}$ inches long. This cross connected the condenser with the pipe and had two plugs for cleaning. The upper $1\frac{1}{2}$ -inch opening of the first tee was bushed to a $\frac{1}{2}$ -inch iron pipe with the lower end capped and extending to about $\frac{3}{4}$ inch from the bottom of the retort. This $\frac{1}{2}$ -inch well held the thermocouple. Pipe fittings were joined with graphite-water paste. This retort was mounted on two $1\frac{1}{4}$ -inch pipe stands, 22 inches high.

CONDENSER. This consisted of a $\frac{3}{4}$ -inch copper tube, 47 inches long, surrounded by a $1\frac{1}{4}$ -inch copper-tube cooling jacket $34\frac{1}{2}$ inches long. The condenser was connected to the horizontal line leading from the retort.

FURNACE SETTING. The retort was enclosed within a setting built out of $\frac{1}{4}$ -inch transite. The top was covered with two semicylindrical sections of 1-inch, 85 per cent magnesia, standard 6-inch pipe covering. Even with these precautions considerable heat was wasted, but this was not regarded as objectionable.

The combusted gases escaped around the vapor neck and kept it sufficiently hot to prevent clogging with condensing tars; the horizontal pipe connecting the vapor neck with the condenser was covered with $\frac{1}{2}$ -inch magnesia pipe lagging to prevent it from clogging.

The gas-fired cast-iron oven burner, $1\frac{3}{4}$ inches in diameter, had a double set of $\frac{1}{16}$ -inch burner holes, $\frac{1}{4}$ inch apart along its length. This was supported $1\frac{1}{2}$ inches below a protecting sheet metal plate on the bottom of the retort with bricks and metal straps around the retort. The protecting sheet metal plate, 4 inches wide and $\frac{1}{16}$ inch thick, was $\frac{1}{4}$ inch below the bottom of the retort and supported from it by iron wire.

COLLECTION OF CONDENSABLE PRODUCTS. The pyrolygneous liquor was collected in a 2000-ml., side-arm Erlenmeyer flask connected at the bottom of the condenser. The noncondensable gas then passed through three 16-ounce baffle bottles to scrub out any entrained liquids still remaining in the gas. The first bottle was empty; in the second and third bottles the gas bubbled through water. The third bottle had a thermometer for obtaining the temperature of the gas going to the gas meter.

TEMPERATURE MEASUREMENT. The temperature of this retort was measured by a calibrated chromel-alumel thermocouple inserted in the thermocouple well described under "retort". The pyrometer used was calibrated every 5°C .

PROCEDURE. Material to be carbonized was charged from one end of the retort in such a way that a free vapor space remained amounting to 20 per cent of the retort volume. The retort was then closed. The retort was heated, and the temperature was controlled by adjusting the gas supply. The data were taken every half hour. When the exothermic point of the carbonization was

reached, as indicated by the large amounts of products given off, the gas supply was throttled so that the distillation would not be too rapid. The run was completed when the flow of noncondensable gases stopped.

When cooled, the retort was opened at both ends, and the charcoal was pushed from one end into a large paper bag at the other end. The pyrolygneous acid was poured into a large graduate and allowed to settle. After several days the amount of aqueous distillate, light tar, and heavy tar were measured and recorded.

CLEANING THE APPARATUS. The vapor neck, connecting lines, and condenser were cleaned by running a $\frac{1}{4}$ -inch capped pipe through them after removing the plugs from the cross and tee. Sometimes a swab soaked with dilute sodium hydroxide and then with water was used. The retort never required cleaning, and the charcoal produced was readily removed.

Analyses

AQUEOUS DISTILLATE. The aqueous distillate was titrated using a pH meter for total acidity, reported as acetic acid. Crude methanol was determined by distilling 50 cc. of the aqueous distillate with 50 cc. of water in a fractionating column with ten bubble plates; 10 cc. were distilled over under 100°C ., and the specific gravity of this sample was determined. The percentage methanol corresponding to this specific gravity was determined from tables.

GAS. The noncondensable gases were analyzed in the Bureau of Mines Orsat apparatus. Carbon dioxide, illuminants, oxygen, carbon monoxide, methane, hydrogen, and nitrogen (by difference) were determined.

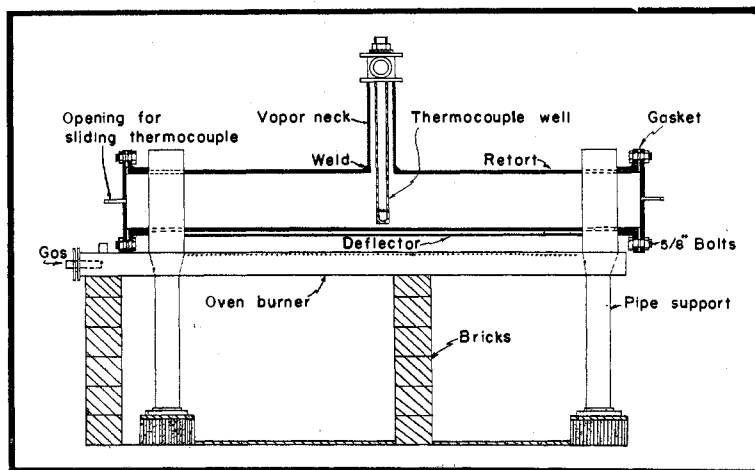


Figure 2. Longitudinal Cross Section of Retort and Housing

TAR. After the tar obtained was weighed, the phenolic and acidic tars were determined. Ten grams of tar were dissolved in ether, and a 10 per cent sodium hydroxide solution was added to extract the phenolic and acidic tars. The aqueous alkaline layer was decanted and acidified with dilute hydrochloric acid, and more ether was added to dissolve the phenolic and acidic bodies again formed by the acidification. The ether layer was separated and evaporated on a hot plate to give the phenolic and acidic tars, which were weighed.



Table I. Summary of Data

Run Number	7	8	9	10	11	12 ^a	13 ^b
Material used							
Compn. (dry basis), %							
Soluble lignin	15.0	33.0	15.0	9.0	100.0	0.0	0.0
Insoluble lignin	29.0	29.0	36.0	43.0	0.0	23.9 ^c	0.0
Total lignin	44.0	62.0	51.0	52.0	100.0	23.9 ^c	0.0
Cellulose	56.0	38.0	49.0	48.0	0.0	76.1 ^d	100.0
Moisture, %	6.5	4.5	4.5	4.5	5.75	6.34	5.49
Weight charged, grams							
Wet basis	2268	2000	2000	1269	1000	1100	453.6
Dry basis	2121	1910	1910	1212	942.5	1030.3	428.7
Total time, hours	10	5	5½	4	5½	4	4½
Maximum temperature, ° F.	714	753	804	730	823	855	840
Yields (dry basis), %							
Fully carbonized material (char-coal)	38.5	45.8	40.0	37.8	55.8	30.3	27.55
Partially carbonized material	7.23	2.4	0.0	0.0	0.0	0.0	0.0
Total aqueous dist. (excluding tars)	27.1	21.0	29.4	30.0	12.35	40.9	47.1
Total tars	8.07	12.3	10.5	11.7	7.15	8.05	6.95
Noncondensable gases (by difference)	19.1	18.5	20.1	20.5	24.7	20.75	18.4
Analysis of aqueous dist., %							
Acetic acid							
Original dry material basis	1.485	0.956	1.413	2.14	0.477	6.31	3.17
Total aqueous dist. basis	4.37	3.71	4.15	6.17	2.59	13.2	5.99
Methanol							
Original dry material basis	0.976	1.074	1.038	0.693	1.92	0.612	0.0
Total aqueous dist. basis	2.87	4.18	2.91	2.00	10.42	1.28	0.0
Phenolic and acidic tars in total tar, %							
Original dry material basis	3.79	5.17	4.21	5.44	3.88	3.30	1.88
Total tar basis	47.0	42.0	40.0	46.3	55.0	41.0	27.0

^a Maple chips.^b Cotton cellulose.^c Extractive-free basis (wood contains 5.65% extractives).^d Includes approximately 25% hemicellulose.

Summary of Experimental Data

In addition to half-hourly temperature readings, liquor and gas analyses were made on samples collected during each 30-minute period. During each run it was thus possible to plot curves against time of temperature run as well as both differential and cumulative amounts of gas and liquid obtained and of the amounts of each of the constituents. This voluminous amount of data and the graphs showing the moment-by-moment conditions of each run are not presented because of

space limitation. In general, the conclusions reached were based on the over-all results in Table I. However the periodic numerical data and graphs illustrated the exothermic reaction and its effect in producing volatile products, and aided in understanding the runs.

In run 7 there was the usual exothermic reaction during the period from 4 to 6 hours for hydrolyzed lignocellulose sample 15/29. The noncondensable gas analyses during this time showed a rapid decrease in carbon dioxide and a rapid increase in methane and hydrogen, particularly after the exothermic reaction was ended.

In run 8 (hydrolyzed lignocellulose 333) the exothermic reaction was somewhat better controlled and resulted in a more regular evolution of products. The gas analyses indicated little change in carbon dioxide and a slight increase in methane, paralleled by a decrease in hydrogen content toward the end of the exothermic reaction.

Hydrolyzed lignocellulose 316 (run 9) was also carbonized with a well-controlled exothermic period. In this case, however, both the carbon dioxide and monoxide in the gases decreased rapidly, while methane and hydrogen increased rapidly.

Carbonization in run 10 (hydrolyzed lignocellulose 345) with a low soluble lignin content resulted in an early exothermic reaction, but this was probably due to a more rapid input of heat to the retort during the first hour. Yields and gas concentrations indicated the same general trend as in run 9.

Run 11 on pure soluble lignin showed a delayed exothermic reaction for this material. The unusual gas analyses showed

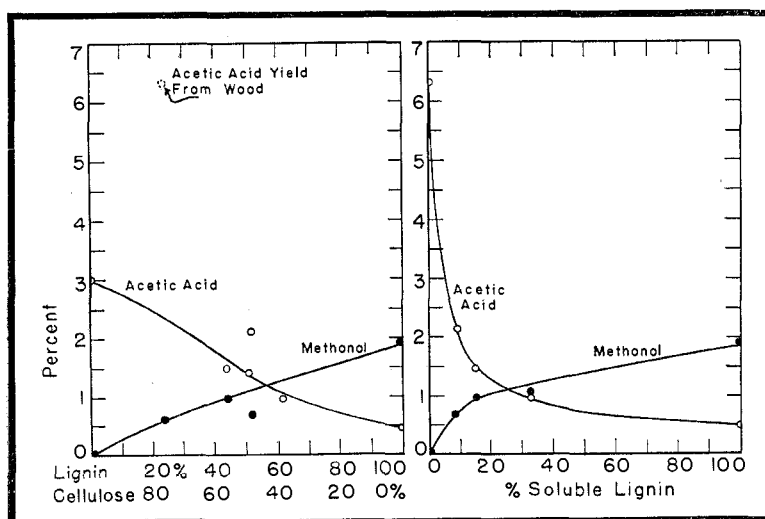


Figure 3. Yields (Per Cent of Dry Material Charged) of Acetic Acid and Methanol as a Function of Composition of Material Charged (Cellulose and Lignin)

Figure 4. Yields (Per Cent of Dry Material Charged) of Acetic Acid and Methanol as a Function of Soluble Lignin Present

large yields of methane and hydrogen in the gas throughout the run, but a rapid increase in carbon monoxide after the exothermic stage was at the expense of these components.

The very regular curves for maple wood (run 12) generally followed the data of Othmer and Schurig (6).

For cotton cellulose (run 13) the exothermic reaction started within the first hour and was practically over by the second hour. During the exothermic stage the carbon monoxide and dioxide concentrations were high, particularly the latter; methane and hydrogen increased considerably after the exothermic reaction was over.

Conclusions

Previous experimenters have reported that cellulose gives a large yield of acetic acid and no methanol, whereas lignin gives a large yield of both acetic acid and methanol. The results obtained here by destructively distilling soluble lignin, various lignocellulose compounds, maple wood, and cotton cellulose contradict many of the previous reports with respect to the source of acetic acid and methanol.

Plots of the various lignocellulose compounds against yield of acetic acid and methanol (Figure 3) show that methanol is derived solely from the lignin. None of the hydrolyzed lignocellulose compounds contained any appreciable amounts of hemicellulose, while the maple chips had a hemicellulose content of about 25 per cent. Since the yield of acetic acid was much higher for the maple wood than for any of the hydrolyzed lignocellulose compounds, it may be said that hemicellulose in the wood is the chief source of acetic acid. This also helps to answer a question raised by Othmer and Schurig (6) because the summation of acetic acid, yields from lignin, hemicellulose, and cellulose did not equal the yield from the wood itself. This is probably due to losses of hemicelluloses during isolation of the various wood components. The low yield of acetic acid obtained from the soluble lignin contradicts other reports that large yields of acetic acid are obtained from lignin. This is probably due to the fact that other experimenters did not use pure lignin but material that contained hemicellulose. The soluble lignin used in this research was tested and found to contain no hemicellulose.

From the plot of percentage soluble lignin against yield of acetic acid and methanol (Figure 4) it is evident that the proportion of soluble lignin present has some effect upon the percentages of acetic acid and methanol obtained from the various lignocellulose compounds. Since the wood itself has no soluble lignin, the run for maple is plotted at 0 per cent.

It was observed from run 11 on soluble lignin and run 13 on cotton cellulose that about twice as much methane and hydrogen are obtained from soluble lignin as from cotton cellulose; more carbon dioxide, carbon monoxide, and illuminants are obtained from cotton cellulose than from soluble lignin. These results are reasonable when the formulas of cellulose and lignin are compared.

From the plot of the summary of yields (Figure 5), it is obvious that soluble lignin gives larger yields of charcoal and noncondensable gases and a lower yield of total aqueous distillate than does cotton cellulose. The various lignocellulose compounds give larger yields of tar than either cotton cellulose or soluble lignin.

Higher yields of acetic acid and methanol from wood as compared with commercial yields check Othmer and Schurig's data (6). It is evident that accurately controlled carbonization is a prime factor in this respect.

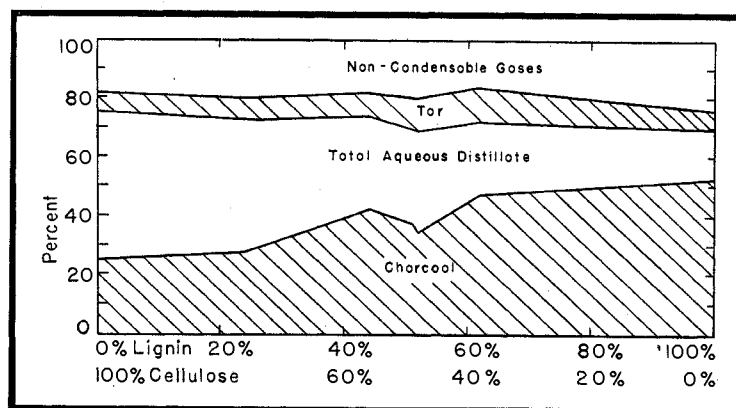


Figure 5. Summary of Yields (Per Cent of Dry Material Charged) as a Function of Cellulose and Lignin in Material Charged

The fully carbonized cotton cellulose obtained in run 13 retained its original fluffy cotton structure. This material might make a suitable filtering material where mechanical strength was not important.

From the low yields of acetic acid and methanol, the destructive distillation of lignocellulose compounds obtained by the hydrolysis of part of the cellulose, hemicellulose, etc., would probably not be profitable.

Soluble lignin produces the largest amounts of phenolic and acidic tars in its total tar, while cotton cellulose gives the smallest. The lignocellulose compounds and maple wood have 40 to 50 per cent phenolic and acidic tars in their total tars. The isolation of phenolic and acidic tars from the total tars would yield an increase in profit. The tar analysis of run 10 showed a larger total yield of phenolic and acidic tars than any other substance destructively distilled in this research. This lignocellulose compound contains a small percentage of soluble lignin; a similar compound is produced as a waste material when soluble lignin is extracted from hydrolyzed lignocellulose compounds. Therefore, the destructive distillation of such a hydrolyzed lignocellulose compound has a possibility of being profitable when its phenolic and acidic tars are considered.

Acknowledgment

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