FACTORS AFFECTING QUANTITATIVE DETERMINATION OF LIGNIN

By 72 Percent Sulfuric Acid Method

April 1932

UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison, Wisconsin
In Cooperation with the University of Wisconsin

FACTORS AFFECTING QUANTITATIVE DETERMINATION OF LIGNIN BY 72 PERCENT SULFURIC ACID METHOD[1]

By

GEORGE J. RITTER, Chemist
R. M. SEBORG, Junior Chemist
and
R. L. MITCHELL, Junior Chemist

A modification of the Ost and Wilkening (3) method for the determination of lignin was published by Mahood (2) of the Forest Products Laboratory in 1922. The modified method was designed for the quantitative determination of lignin in wood. Since its publication, Mahood's method has been modified at various times. The need for changes became necessary soon after 1922, when such materials as Cross and Bevan cellulose, chemical pulps, and flax were analyzed for their lignin content. More recently the need for additional changes became apparent when Sherrard and Harris (4) found that slightly elevated temperatures alter the physical and the chemical nature of lignin prepared by the 72 percent sulfuric acid method.

These modifications may be classified under the following headings: (1) treatment of samples with alochol-benzene; (2) ratio of acid to sample; (3) extraction of the sample with hot water; (4) duration of contact of sample with 72 percent sulfuric acid; (5) temperature of the mixture containing 72 percent sulfuric acid and wood; and (6) duration of hydrolysis.

Pretreatment of Samples

To avoid the presence of foreign materials in the lignin residue, pretreatment of the sample is necessary. The oils, resins, fats, and waxes are removed by extracting the sample with a minimum boiling-point solution of alcohol-benzene as recommended by Mahood (2).

Bray, in determining lignin in chemical pulps (1), found the alcohol-benzene extraction unnecessary in most pulps, since any fatty or resinous materials remaining after the pulping process caused no interference with the subsequent lignin determination. Later the extraction was omitted in the determination of lignin in all chemical pulps. Recently it has been found, however, that the extreme difficulty experienced in filtering and washing the lignin residue from sulfite pulps which retain resins and fats may be largely overcome by pretreating such pulps with the alcohol-benzene solvent.

---

[1]Published in Industrial and Engineering Chemistry, April 15, 1932.
R969

Ratio of Acid to Sample

As originally adopted by the Forest Products Laboratory, the method specified 12.5 cc. of 72 percent sulfuric acid per 2 grams of sawdust. That ratio of acid to sample is sufficient, but it requires considerable time for triturating the wood-acid mixture. If the ratio of the acid to the sawdust sample is increased, as advocated later in this paper, the trituration can be accomplished with greater ease and in less time. Further, when the method is employed for the analysis of chemical pulps, which have a much higher cellulose content than wood, it is found necessary to increase the acid-sample ratio in order to dissolve the carbohydrates (1).

Extraction of Sample with Hot Water

If the alcohol-benzene extracted residue is extracted with hot water and dried before treating with 72 percent sulfuric acid, very noticeable effects are observed in some cases, as is shown in Table 1. The lignin residue obtained is lighter in color, the yield lower, and filtration and washing facilitated.

Apparently these effects are due to the presence, in some woods, of extractives which are insoluble in alcohol-benzene but soluble in hot water. Further, these extractives are insoluble in sulfuric acid or converted into insoluble products by the acid treatment.

Duration of Contact of Sample with 72 Percent Sulfuric Acid

The time during which the sample and the concentrated acid are in contact has a direct bearing on the quantity of the lignin residue. Time must be allowed for the carbohydrates to dissolve, but continued exposure appears to caramelize some of the dissolved carbohydrate material partially rendering it insoluble. The insoluble material is thus included in the lignin residue. The amount of partially decomposed carbohydrate material and the color of the lignin residue increases with the time of contact between the sample and the concentrated acid. Relationships between times of exposure of the sample to the concentrated acid and lignin yields are shown in Figure 1. A period of 2 hours has been adopted for the duration of contact of the sample with the 72 percent sulfuric acid.

Temperature of Concentrated Acid and Wood Mixture

Room temperature was originally specified for dissolving the cellulosic material in the 72 percent sulfuric acid. Since there is usually a wide range in room temperatures during the various seasons of the year, and since Sherrard and Harris (4) have found that the amount and the properties of lignin are altered by slight variations in temperature during its

isolation, it seemed advisable to study the temperature factor. From the results recorded in Figure 1, it may be noted that the 17-hour treatment of the sample with 72 percent sulfuric acid indicates that yields from 22.3 to 28.3 percent are obtained at temperatures ranging from 17° to 35° C. Shorter treatments of 1 and 2 hours at the same temperatures indicate that yields from 21.5 to 22.5 percent are obtained. The 1-hour treatment shows, as a result of undissolved carbohydrates, a rise in yield in going from 15° to 10° C. The 2-hour treatment at 20° C. has been chosen, therefore, in order to insure complete solution of the carbohydrates with minimum decomposition. If these conditions are not maintained, lignin yields may be obtained from refined pulps or from Cross and Bevan cellulose which may be due largely to partially decomposed carbohydrates, as shown by Sherrard and Harris (4). Darker color of the lignin as well as increased yields accompany increasing temperatures of the acid-wood mixture.

Duration of Hydrolysis

After the dissolving of the carbohydrates is completed in the 72 percent sulfuric acid, enough water is added to the wood-acid mixture to obtain a 3 percent acid solution. During the dilution, a part of the modified carbohydrates in the form of dextrin-like material is reprecipitated. The mixture must therefore be boiled in order to hydrolyze and render soluble all the carbohydrates and at the same time coagulate the finely divided insoluble ligneous material so that filtering and washing of the residue may be facilitated.

Working with several woods, it was found that 4 hours are sufficient for the hydrolysis of the carbohydrate portion, giving a clear filtrate. For shorter periods the filtrate from some woods was cloudy and gave a brown residue, whereas some of the woods examined did not require such a long period. Some types of materials to be examined in the future may require even longer periods, in which event the 4-hour period should be modified to suit the conditions.

Procedure for Determination of Lignin in Wood

Since it has been shown that certain factors affect the lignin determination, it is suggested that the sulfuric acid method for the determination of lignin in wood be modified to read as follows:

Approximately 2 grams of air-dried sawdust (60 to 80, or 80 to 100 mesh) are weighed in a tared alundum crucible. The crucible and its contents are dried to constant weight at 105° C., cooled, and weighed. The material is then extracted for 4 hours in a Soxhlet apparatus with a minimum boiling solution of alcohol-benzene. The solvent is removed by suction, the residue washed with alcohol by suction to remove the benzene,

and then extracted with 400 cc. of hot water in a water bath for 3 hours, filtered, washed with hot water, then with alcohol, and finally dried. (Washing the residue with alcohol aids in the removal of the sawdust from the crucible after drying.) The dried residue is transferred to a glass-stoppered weighing bottle, and is well mixed with 25 cc. of 72 percent sulfuric acid at 20° C., and maintained at that temperature for 2 hours. The resulting mixture is transferred to an Erlenmeyer flask, diluted with water to make a 3 percent acid solution, and then boiled for 4 hours under a reflux condenser. The hydrolyzed residue is filtered on a tared alundum crucible, washed free of acid by means of hot water, dried, and weighed. The lignin content is calculated on the basis of the oven-dry sample.

In case a correction for ash is desired, transfer the lignin residue to a tared platinum dish and ash in the usual way.

In the determination of lignin in chemical pulps, 40 cc. of 72 percent sulfuric acid should be used for dissolving the carbohydrates present in a 2-gram sample. The water extraction may be omitted with all chemical pulps and the alcohol benzene may be omitted with alkaline-cooked pulps.

If large quantities of lignin are prepared at one time, it is difficult to control the temperatures developed during the mixing of the acid and the sawdust. It is advisable, therefore, to use a lower concentration of acid and mix it with the sawdust at a lower temperature than specified above. Sherrard and Harris (4) have found that a 70 percent sulfuric acid mixed with sawdust at 10° C. is satisfactory.

Results obtained from lignin determinations in several woods according to the foregoing revised method are recorded in the last column of Table 1. The effect of temperature on the lignin yields may be noted by comparing columns 1 and 2; the effect of hot-water extraction, by comparing columns 2 and 3.

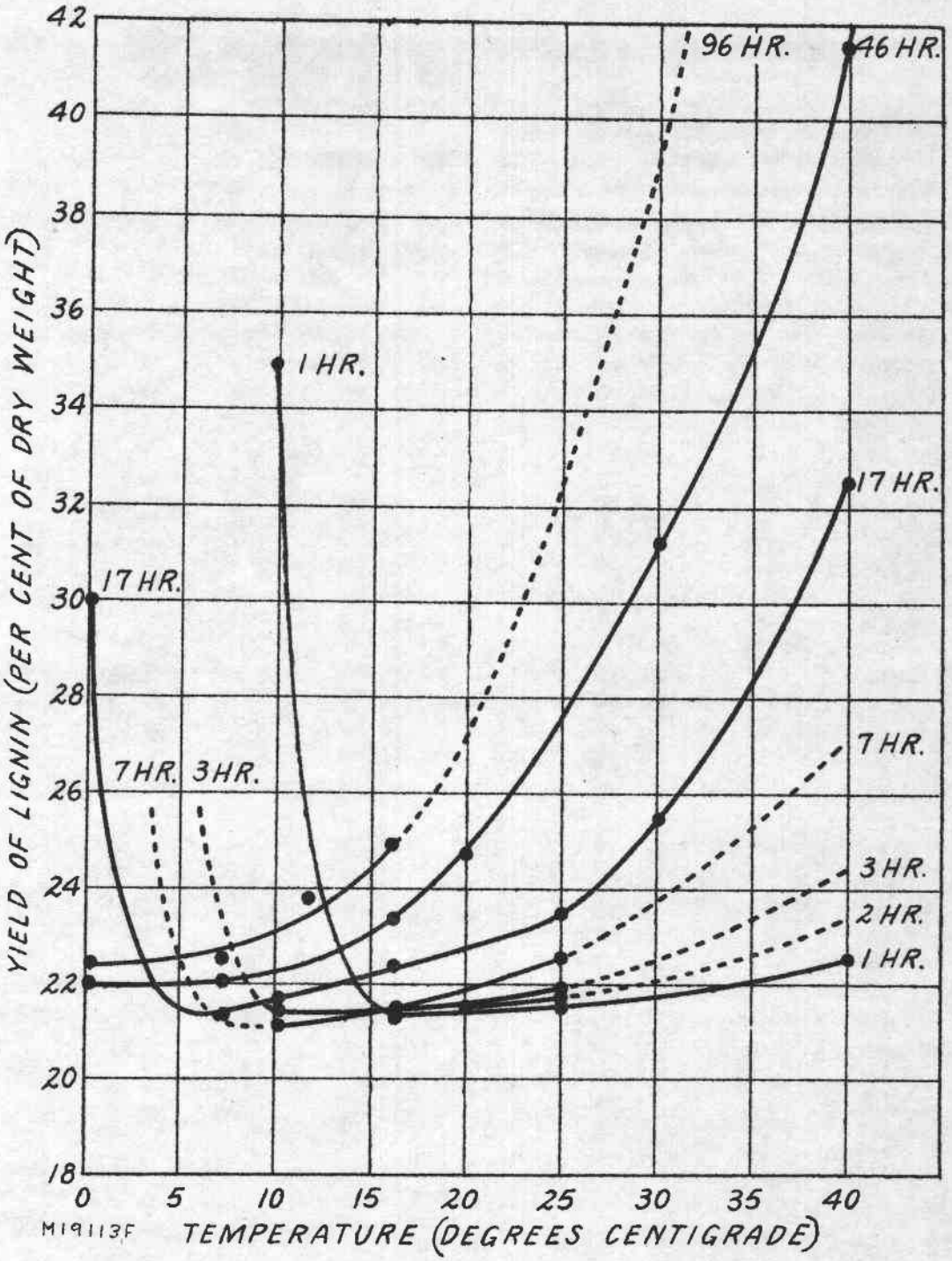
LITERATURE CITED

(1) Bray, M. W., Paper Trade J., 87, 59-68 (1928).
(2) Mahood, S. A., and Cable, D. E., J. Ind. Eng. Chem., 14, 933 (1922).
(3) Ost, H., and Wilkening, L., Chem.-Ztg., 34, 461 (1910).
(4) Sherrard, E. C., and Harris, E. E., Ind. Eng. Chem., 24, 103 (1932).

Table 1.--Effect of temperature and extraction with hot water on lignin yields of 5 woods

Species	Treatment with acid[1] for 17 hours at room temperature	Treatment with acid[1] for 2 hours at 20° C.	
		Without hot-water extraction	With hot-water extraction
Sugar maple	23.15	21.40	21.05
	23.50	21.70	21.20
	23.05	21.45	21.10
	23.25	---	21.35
	Av. 23.24	21.52	21.18
White spruce	27.00	26.00	25.90
	27.50	25.95	25.90
	27.70	26.00	25.95
	27.35	26.30	25.85
	Av. 27.39	26.06	25.90
Incense cedar	35.85	34.80	33.85
	36.40	34.25	33.80
	36.25	34.05	33.75
	36.10	34.10	33.25
	Av. 36.15	34.30	33.66
Catalpa	20.32	17.67	17.23
	20.35	18.12	17.32
	20.55	18.04	17.31
	20.38	18.40	17.34
	Av. 20.40	18.06	17.30
Mesquite	30.20	27.95	24.70
	30.35	28.00	24.70
	30.60	27.75	25.10
	30.55	27.15	24.50
	Av. 30.42	27.71	24.75

[1]72 percent sulfuric acid.



EFFECT OF TIME AND TEMPERATURE ON LIGNIN YEILDS IN SUGAR MAPLE WITH 72 PER CENT SULPHURIC ACID