THE INTERDEPENDENCE OF THE LIGNIN CONTENT AND ELECTRICAL PROPERTIES OF WOOD

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ABSTRACT

A linear relationship was found to exist between the percentage of acid-insoluble lignin content and both the permittivity and DC conductivity of vacuum-dried woods, woods conditioned at 65% relative humidity, and in both of the two major grain directions. This study shows that dielectric measurements could be developed into a nondestructive analytical tool for estimating acid-insoluble lignin content in woods.

Additional keywords: Permittivity, DC conductivity, Klason lignin, nondestructive analysis, specific gravity.

INTRODUCTION

The interdependence of certain properties of wood and its components, such as density, fiber length, interfiber bonding (Gallay 1961), and permittivity (Calkins 1950) is generally recognized. Since the individual properties of wood and wood components are very complicated in nature, the recognition of the interdependence between these properties is in many cases, only qualitative (Gallay 1961).

In determining the physical and chemical properties of wood and its components, submicroscopic structure plays an important part. Each wood component contributes to electrical polarization differently because of differences in polarity of molecular chains and segments, individual structures, and orientation in a field. For example, cellulose consists of crystalline and noncrystalline zones. Cellulose molecules are laterally bound by secondary valence forces, particularly hydrogen bonding, and the hydroxyl groups resulting from this bonding are polar and respond to the application of an electric field in a certain fashion. It is well recognized that lignin is noncrystalline and this component in wood contributes to electric polarization in quite a different manner from cellulose (Venkateswaran 1972).

Previous electrical measurements (Venkateswaran 1972) on pellets prepared from a mixture of milled wood cellulose and milled wood lignin of varying proportions showed that a linear relationship existed between the permittivity and percentage of lignin in the pellet.

The present work is an extension to woods covering a wide range of acid-insoluble lignin contents (15–33%) to see if a similar linear relationship exists, and if so, whether the lignin content in wood could be measured nondestructively by dielectric measurements. It is assumed that the geometry of samples of different species prepared in the same grain direction is equal.

Explanation of specific permittivity

The ratio of the capacitance of a condenser with a dielectric to its geometrical capacitance is called the relative permittivity of the material. For a porous substance, this ratio is not the relative permittivity of the material itself since it depends upon the amount of voids in the substance. This ratio for the substance itself is termed the specific relative permittivity. This is referred to here as 'the specific permittivity' (Venkateswaran 1972).

EXPERIMENTAL PROCEDURE

Preparation of samples

For electrical measurements, wood samples between 0.5 and 1 mm thick and 5 cm

TABLE 1. *Species of woods studied in this work and their densities*

Identification number	Common name	Specific name	Density[1] (g/cc)	Acid insoluble lignin content (%)
1	Trembling aspen	*Populus tremuloides* Michx.	0.41	18.2
2	Yellow birch	*Betula alleghaniensis* Britt.	0.58	22.5
3	Douglas-fir	*Pseudotsuga menziesii* (Mirb.) Franco	0.50	29.0
4	Red pine	*Pinus resinosa* Ait.	0.39	27.7
5	Basswood	*Tilia americana* L.	0.41	16.3
6	Manitoba maple	*Acer negundo* L.	0.50	23.8
7	White elm	*Ulmus americana* L.	0.55	28.5
8	Sugar maple	*Acer saccharum* Marsh.	0.67	25.0
9	White spruce	*Picea glauca* (Moench) Voss	0.43	25.9
10	Red oak	*Quercus rubra* L.	0.62	24.0
11	Eastern white pine	*Pinus strobus* L.	0.42	26.7
12	Black walnut	*Juglans nigra* L.	0.56	27.2
13	Beech	*Fagus grandifolia* Ehrh.	0.62	22.7
14	Eastern hemlock	*Tsuga canadensis* (L.) Carr.	0.40	32.5
15	Red juniper	*Juniperus virginiana* L.	0.52	35.0

[1] Vacuum-dried specimens.

in diameter were prepared from logs submerged in water. Samples were prepared such that the field could be applied along and perpendicular to the grain direction. Measurements were made in triplicate, using three specimens of each species of wood. Table 1 gives a complete list of the names and vacuum-dried densities of the woods analyzed in this study. These same samples were used for chemical analyses and their acid-insoluble lignin contents are also indicated in Table 1.

Electrical and chemical measurements

Capacitances of all wood samples (5 cm diameter, 0.5 mm thick) at 10^4 Hz were measured using a GR 1615A capacitance-conductance bridge. The DC conductivities (k_{dc}) were computed from the resistances (determined by a 610C Keithley Electrometer) and linear dimensions of all the samples. The electrode gap required to calculate the permittivity (ϵ) and density (d) of each sample under test was obtained with an electrode system made in this laboratory (a modification of Calkin's electrode arrangement (Venkateswaran 1972)).

The electrical properties of samples dried at room temperature and in vacuum (less than 10^{-4} Torr.) for at least 16 h were measured first. The same samples were then conditioned at 20 C and 65% relative humidity in a controlled humidity room and the same properties were again determined.

Lignin content was determined following Tappi standard T13 m-45. The hemicellulose content in various woods was determined first by isolating holocellulose and then determining the hemicellulose fractions, following the method of Wise et al. (1945). Lignin and hemicellulose fractions are expressed in percentages of the total moisture-free weight of wood.

DATA ANALYSIS

To compare the electrical properties of wood substance in two different pieces or species of wood, the measured parameters should be corrected to a common density, since the electrical properties of a porous material such as wood vary with the amount

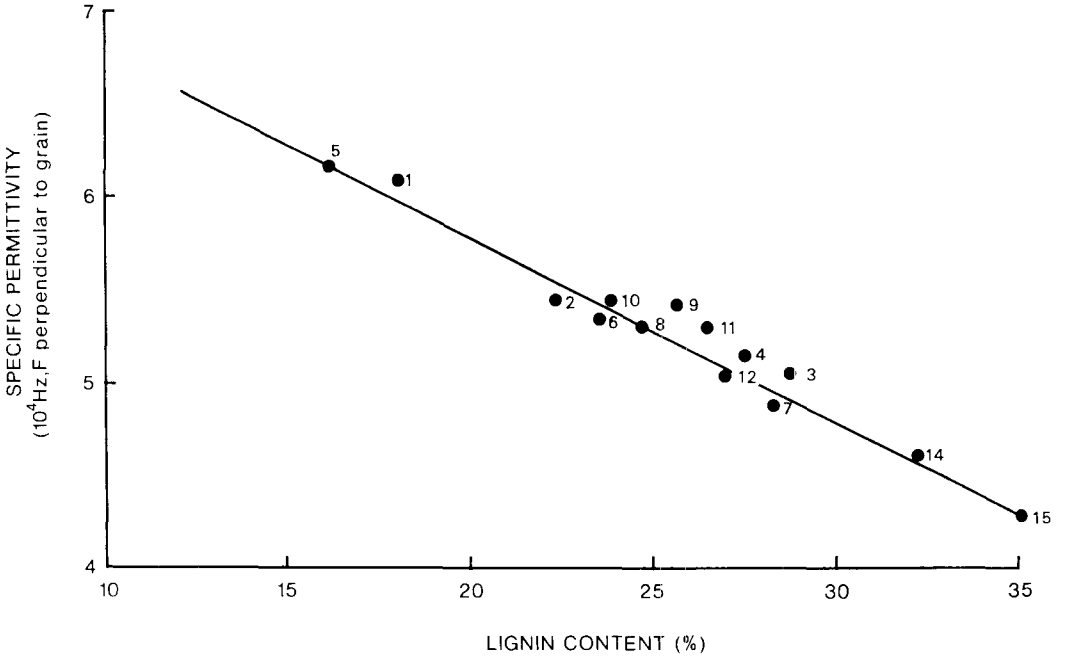

FIG. 1. Relationship between acid-insoluble lignin content and specific permittivity of woods. (See Table 1 for species identification.)

of void space in a given volume. A correction for the permittivity to an arbitrary density may be made using equation (1). In this study a correction to a density of 1.53 g/cc was made (Venkateswaran 1965):

$$\epsilon_1 = (\epsilon_o - 1) \frac{d_1}{d_o} + 1 \qquad (1)$$

where ϵ_1 is the specific permittivity [Venkateswaran 1969] at the density of wood substance d_1 ($= 1.53$ g/cc) and ϵ_0 is the measured permittivity at density d_0 in g/cc.

Strictly speaking, the conductivity values should also be corrected to the density of wood substance. A previous study (Venkateswaran 1970) in this laboratory showed that density and conductivity of various woods are not linearly related, that the variation of resistivity with density differs from species to species, and that a correction for density shows that the effect of density on log conductivity is very small, ($\simeq 2.0\%$). Consequently, the correction due to density has been neglected.

RESULTS AND DISCUSSION

To illustrate the interdependence of the lignin content and electrical properties of wood, permittivity and DC conductivity are used. Figure 1 shows the specific permittivity of vacuum-dried woods (with a 10^4 Hz field applied perpendicular to the grain) plotted against the percent acid-insoluble lignin in wood. Figure 2 gives the relation between lignin content and DC conductivity of these woods. The numbers on these figures correspond to the number assigned to each species in Table 1.

Wood contains 15–40% lignin (Berzins 1966); this study covered the range 15–35%. For this range, the relationships between electrical parameters at 10^4 Hz and 20 C and the percent lignin content may be empirically expressed as:

$$\epsilon^1 = -mL + \epsilon_1^1 \qquad (2)$$

$$k_{dc} = m_1 L + k_1 \qquad (3)$$

where ϵ^1 and k_{dc} are the specific permittivity

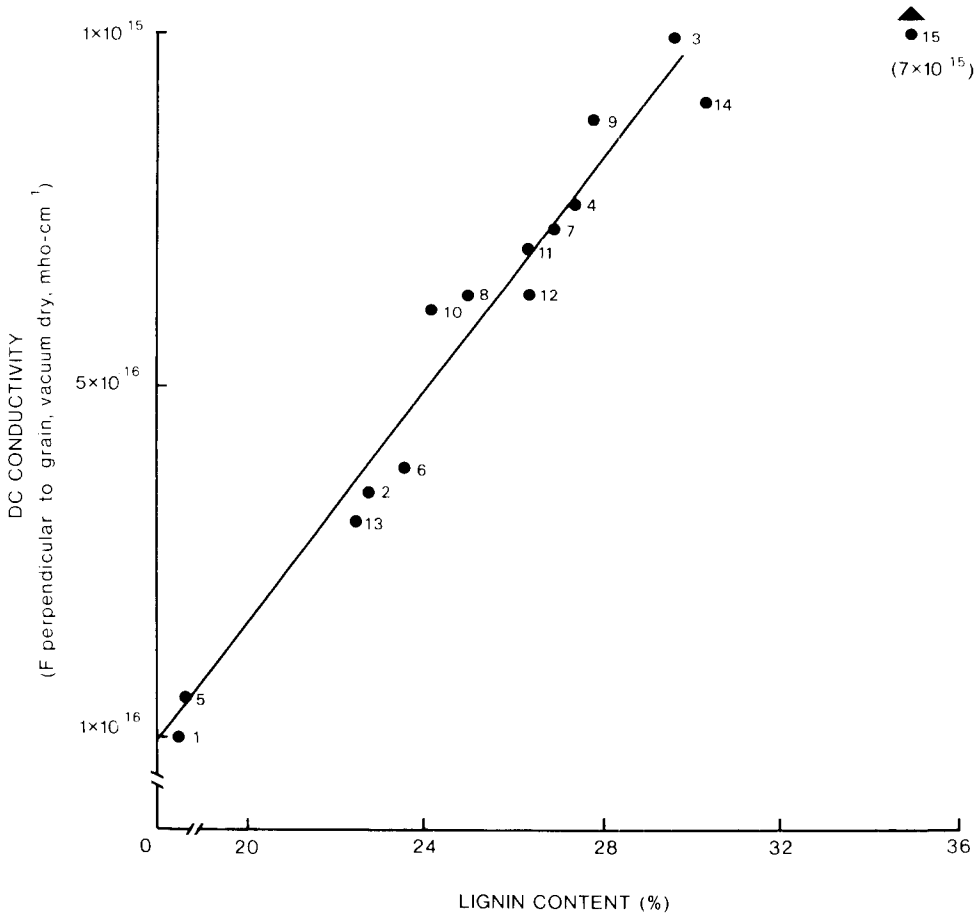

FIG. 2. Relationship between acid-insoluble lignin content and DC conductivity of woods. (See Table 1 for species identification.)

and DC conductivity of wood at a lignin content in the range studied, L the percent lignin in wood, m the slope (determined by regression analysis) and $\epsilon_1{}'$ and k_1 the specific permittivity and DC conductivity of wood at 15% lignin content (Figs. 1 and 2). The minus sign in Eq. (2) indicates a negative correlation.

Note that Eq. (2) or (3) is applicable only for a range of 15–35% lignin. A general equation relating 0–100% lignin and the corresponding permittivities was not attempted since wood having lignin content less than 15 or more than 40% does not commonly exist in nature and consequently extrapolated values could not be compared with experimental results.

The correlation coefficient and standard errors of estimate of the interdependence between electrical properties and chemical composition are given in Table 2. These values are mostly quite high, showing that the association between these quantities is highly significant.

The specific permittivity and conductivity of wood samples with the field parallel to the grain direction and of the same samples conditioned at 65% relative humidity also correlated well with lignin content. Coefficients of correlation of these results are included in Table 2.

There was little correlation (0.2) between hemicellulose fraction and specific permittivity of the woods studied. No relation-

TABLE 2. *Correlation coefficients of interdependence of electrical properties and chemical composition of woods*

Wood Properties	Correlation Coefficient	Standard Error of estimate
1. Lignin - specific permittivity ($F_{\perp}$[1] vacuum-dried samples)	0.985	0.10
2. Lignin - specific permittivity ($F_{\parallel}$[2] vacuum-dried samples)	0.935	0.21
3. Lignin - specific permittivity ($F_{\parallel}$ at 65% relative humidity)	0.932	0.36
4. Hemicellulose - specific permittivity ($F_{\parallel}$ vacuum-dried samples)	0.20	--
5. Lignin - DC conductivity ($F_{\perp}$ vacuum-dried samples)	0.986	0.45
6. Lignin - DC conductivity ($F_{\perp}$ at 65% relative humidity)	0.967	0.56

[1] $F_{\perp}$ = perpendicular to the grain

[2] $F_{\parallel}$ = parallel to the grain

ship was observed between ash content (Berzins 1966) and electrical properties of vacuum-dried woods. In the vacuum-dry condition, small percentages of metallic elements in wood are randomly distributed, and this distribution has little or no effect on capacitance or conductance.

ANALYSIS OF ERROR IN DIELECTRIC AND ACID-INSOLUBLE LIGNIN DETERMINATIONS

The dielectric measurements involved measuring the diameter, thickness, and vacuum-dry weight of a sample, and its capacitance and conductance. The diameter and thickness of the sample were determined within ±0.1 mil (±0.00254 mm). The sample was weighed on a balance of 0.01 mg sensitivity. Errors in capacitance were ±0.01% and in conductance 1.0% of the dial readings for a sample. With these measured values, the error in calculated permittivity and conductivity is estimated to be less than 0.5% (Venkateswaran, to be published).

The reproducibility of permittivity on the same sample and the variation of permittivity between samples prepared from different logs of the same species are given in Table 3.

Acid-insoluble lignin values of all the samples determined separately are also included in this Table. The standard deviation of acid-insoluble lignin values is higher than that of permittivities. This difference could arise from the errors introduced in various experimental steps (several washings and filterings) involved in the acid-insoluble lignin determination.

Acid-insoluble lignin in a piece of wood is usually determined by preparing a homogeneous mixture of ground wood passing through a 40-mesh screen and retained on a 60-mesh screen. Lignin content determined in duplicate from this homogeneous mixture for beech agrees within 0.5%, while lignin contents of beech samples prepared from different logs show a higher variation (Table 3). The lignin content of wood

TABLE 3. *Density, permittivity, and acid-insoluble lignin content of beech*

Sample number	Density (g/cc)	Measured permittivity	Permittivity corrected to 1.53 g/cc	acid insoluble lignin (%)	Remarks
A_1	0.618	2.819	5.50	20.9	same sample
A_2	0.618	2.815	5.49	20.8	samples from one log
B	0.615	2.813	5.51	21.1	
C	0.620	2.822	5.48	21.0	
Standard deviation of A_1 to C			0.01	0.12	
D	0.580	2.702	5.49	22.0	
E	0.584	2.698	5.45	21.4	samples from another tree of the same species
F	0.575	2.682	5.48	21.3	
G	0.581	2.685	5.44	21.6	
Standard deviation of D to G			0.02	0.26	
Standard deviation of all samples			0.02	0.37	

from different trees of the same species, and from trees of different species varies as much as 2–7% (Brauns and Brauns 1960; Berzins 1966).

A recent combination and revision of the Tappi methods T 13m-54 and T 222m-54 proposes that the determination of lignin content (from 2.6 to 19.1%) in sulfate pulps should have repeatability of 0.17; for the determination of lignin content in sulfite pulps (from 6.5 to 28.0%), the repeatability should be 0.48%. Acid-insoluble lignin fractions reported in Table 3 are within these limits.

Since capacitance measurements are very sensitive, any difference in lignin present in wood would be reflected in the electrical polarization. An added advantage is that electrical measurements do not destroy samples either chemically or mechanically.

The standard deviations in Table 3 show that the accuracy of either the permittivity measurement or the acid-insoluble lignin measurement (±1.5%) cannot be improved appreciably by increasing the number of determinations. One reason for the deviation in lignin content estimated by the two methods may arise from small variations in the geometry of the samples having one grain direction; this variation is sensitive to electric polarization. Grinding the wood to a particular particle size and preparing a pellet from it would reduce this geometry problem. This mechanical treatment has been found to alter the fine structure of wood (Venkateswaran 1972).

It is also possible, as in the determination of fine structure of cellulose by permittivity measurements (Verseput 1951), that the determination of lignin in wood by electrical polarization would be different from that determined by a chemical method, since polarization is uniquely determined by the molecular structure in the original material. The estimate of lignin content obtained by the sulfuric acid method need not be equivalent to that existing in a piece of wood before chemical treatment. This was pointed out several decades ago by Campbell and McDonald (1952), who found that the estimation of percent holocellulose as [100– (sulfuric acid lignin)] was in error because of the existence of "modified lignin" not estimated by the sulfuric acid method. Our study shows that dielectric measurement could be developed into an analytical tool to estimate lignin content in natural wood. This method of measuring lignin is rapid and nondestructive.

The three major constituents of the wood cell wall are cellulose, hemicellulose, and lignin, and these constituents are in close physical association. Inasmuch as their

chemical and physical properties overlap, sharp separation of the constituents is a matter of extreme difficulty. There exists no extraction method by which one of the components of wood can be removed quantitatively without affecting the others. Therefore, a certain amount of scattering of results is to be expected. As in the case of the interdependence of density, fiber length etc. (Gallay 1961), the interdependence of the chemical composition and electrical properties is also not absolute.

CONCLUSIONS

There are linear correlations between Klason lignin content and permittivity, and DC conductivity of wood. These relationships are valid for both of the major grain directions in wood. The correlation coefficients show that the association between these quantities is highly significant. These relationships also are valid for woods conditioned at 65% relative humidity. There is little association between the hemicellulose fraction and permittivity of woods.

Dielectric measurements can be used as a nondestructive analytical tool to estimate the lignin content of wood. Such an estimate by electrical polarization may not be identical to that determined by a chemical method since in permittivity measurements the sample is not destroyed mechanically or chemically, whereas in the Klason method, chemical modification of lignin takes place during the separation.

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