EFFECT OF LIGNIN CONTENT AND EXTRACTIVES ON THE HIGHER HEATING VALUE OF WOOD

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ABSTRACT

As part of a study of the charring rate of wood, I determined the higher heating values (gross heat of combustion) and the chemical composition of samples from four hardwoods and four softwoods. The higher heating value of wood was correlated with lignin and extractive contents. There was a highly significant linear correlation between the higher heating value of the extractive-free wood and lignin content. Equations are presented that can be used to determine the higher heating value of extractive-free wood when the Klason lignin content is known. The equations should be useful to those interested in using a variety of species of wood as fuel.

Keywords: Gross heat of combustion, wood, lignin, heating values.

INTRODUCTION

As part of a study of the charring rate of wood, I determined the higher heating values (gross heat of combustion) and the chemical composition of eight species of wood in tests of both unextracted wood samples and samples of wood extracted with ethanol/benzene. In this paper, the higher heating values obtained for the wood samples are compared with their Klason lignin and extractive contents. The higher heating values include the latent heat of the water vapor products of combustion because the water vapor was allowed to condense to liquid water.

MATERIALS AND METHOD

Materials

The eight species consisted of four softwoods and four hardwoods. The four softwoods were Engelmann spruce *(Picea engelnzanni),* western redcedar (*Thuja plicata),* southern pine *(Pinus* sp.), and redwood *(Sequoia sempervirens).* The four hardwoods were hard maple *(Acer* sp.), yellow-poplar *(Liriodendron tulipifera),* red oak *(Quercus* sp.), and basswood (*Tilia* sp.). Samples were ground from three boards of maple, six boards of pine, and four boards of each of the other species. Each sample contained a mixture of materials from different sections of the board.

Chemical composition

The Forest Products Laboratory's Analytical Laboratory determined the percent Klason lignin and percent extratives of the ground sample from each board. A portion of each sample was extracted with ethanol/benzene (ASTM 1984), and Klason lignin was determined as the insoluble residue after hydrolysis of the wood

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TABLE 1. ***Average heating values and chemical composition of wood samples.***

Species	Klason lignin	Extractive	Higher heating values	
			Unextracted wood	Extractive-free wood
	% of oven-dried wood		*Btu/lb*	
Softwoods				
Engelmann spruce	26.9	2.4	8,650	***8,570***
Western redcedar	30.8	7.8	8,890	8,800
Southern pine	26.8	5.4	8,890	8,610
Redwood	33.8	8.2	9.120	8,940
Hardwoods				
Maple	21.7	5.3	***8,450***	8,450
Yellow-poplar	20.5	3.8	***8,440***	8,360
Red oak	22.5	6.4	***8,590***	8,410
Basswood	18.1	6.7	***8,590***	8,290

with *72%* sulfuric acid (Effland 1977). The acid-soluble lignin content of one ground sample from one board of each hardwood species was determined spectrophotometrically.

Determination of higher heating values

The higher heating values of unextracted and extractive-free samples were determined by forming the samples into pellets weighing approximately 1 g each and burning the pellets in an adiabatic oxygen bomb calorimeter (Parr 1241 automatic adiabatic calorimeter and Parr 1108 oxygen bomb). Initial moisture contents (oven-dry basis) were 5 to 7% for the unextracted wood samples and 1 to 4% for the extractive-free samples. Computations of the higher heating values included corrections for the oven-dry weight of the samples and the combustion of the fusing wire. I made no corrections for nitric acid or sulfuric acid (Barnes and Sinclair 1984; Harris 1984) or for the differential heat of absorption of the bound water (Hawley and Wise 1926). Generally, only one test per test material was made.

RESULTS

Higher heating value of unextracted wood

The average higher heating value of the unextracted wood was 8,890 British thermal units per pound (Btu/lb) for the four softwoods and 8,529 Btu/lb for the four hardwoods (Table 1). For the individual samples of each species, the heat of combustion ranged from 8,600 to 9,260 Btu/lb for the softwoods and from 8,410 to 8,880 Btu/lb for the hardwoods. As discussed by Baker (1983), values reported for a given species reflect only the samples tested and not the entire population of the species. Although the values reported in this paper are lower than some values for resinous softwoods reported in the literature, my results were generally consistent with other reported values (Harris 1984; Ince 1979; Parr and Davidson 1922).

Using linear regression analysis, I compared the higher heating values with the chemical composition data. Linear regression of the higher heating value of the

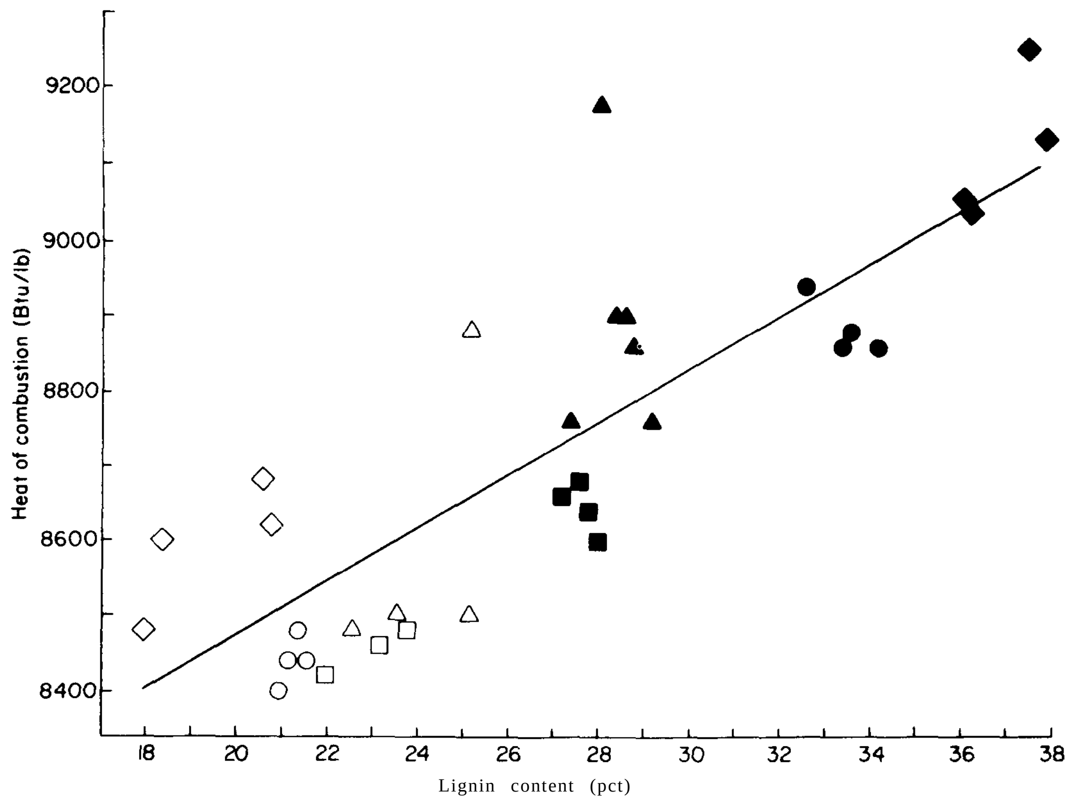

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FIG. 1. Higher heating values of virgin wood versus percent lignin content. ■ = Engelmann spruce, ● = western redcedar, ▲ = southern pine; ◆ = redwood, □ = maple, ○ = yellow-poplar, △ = red oak, and ◇ = basswood. Line is based on linear regression of the data. (ML86 5389)

unextracted wood with the lignin content (extractive-free basis) resulted in a square of the correlation coefficient (R^2) of 0.70 (Fig. 1). The addition of extractive content to the linear regression equation improved the R^2 to 0.76. For the model including the lignin content and extractive content, the regression equation is

$$h_o = 7{,}696 + 32.0X_\ell + 28.4X_E \qquad (1)$$

where

h_o = higher heating value of unextracted wood (Btu/lb)
X_ℓ = Klason lignin content (% oven-dry, extractive-free wood)
X_E = extractive content (% oven-dry wood).

The standard error of the estimates is 123, and the standard errors of the parameters are 113 for the intercept, 4 for the X_ℓ coefficient, and 10 for the X_E coefficient.

Higher heating value of extractive-free wood

The average higher heating value of the extractive-free samples was 8,730 Btu/lb for the softwoods and 8,380 Btu/lb for the hardwoods (Table 1). For the extractive-free wood, the higher heating value was highly correlated with lignin content (Fig. 2). For all eight species, the linear regression equation is

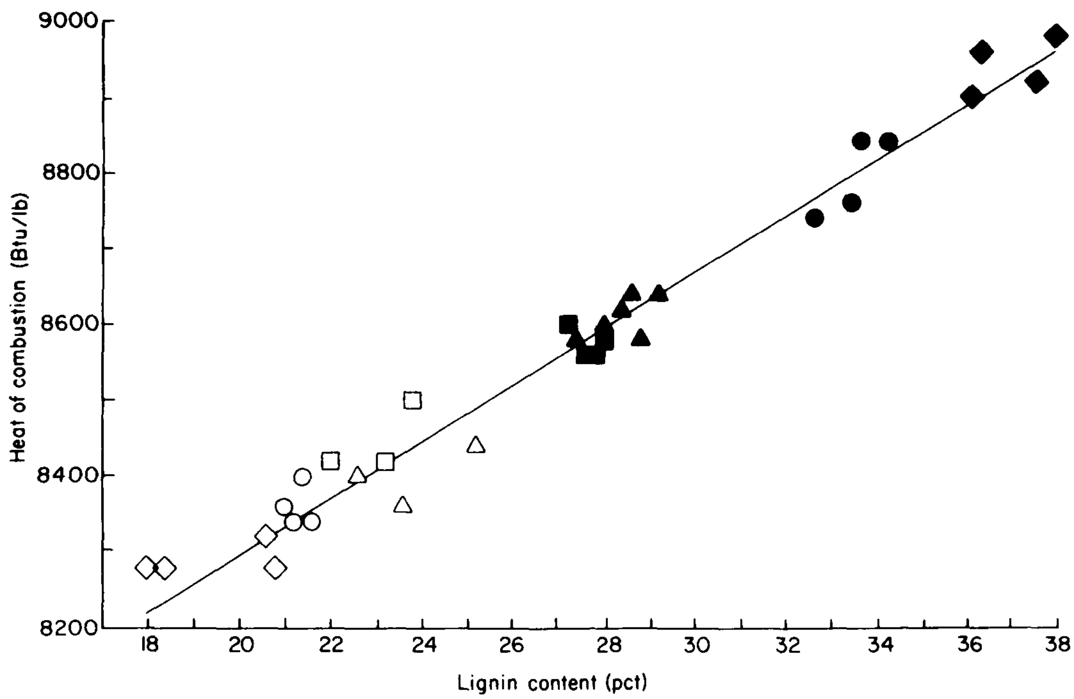

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FIG. 2. Higher heating values of extractive-free wood versus percent lignin content. ■ = Engelmann spruce, ● = western redcedar, ▲ = southern pine; ◆ = redwood, □ = maple, O = yellow-poplar, △ = red oak, and ◇ = basswood. Line corresponds with regression Eq. (2). (ML86 5388)

$$h_e = 7,572 + 36.7X_\ell \quad (2)$$

where

h_e = higher heating value of extractive-free wood (Btu/lb).

For Eq. (2), the R^2 *is* 0.97. The standard errors are 37 for the estimate, 32 for the intercept, and 1 for the X_ℓ coefficient. There were significant differences in the slopes for the hardwood and softwood data.

For the softwoods, Klason lignin accurately reflects the total lignin content of the wood. For the four softwoods, the regression equation is

$$h_e = 7,500 + 39.0X_\ell \quad (3)$$

For Eq. (3), R^2 *is* 0.96. The standard errors are 30 for the estimate, 60 for the intercept, and 2 for the X_ℓ coefficient.

However, hardwood lignins are partially soluble in 72% H_2SO_4, and the acid-soluble portion may comprise 10 to 20% of the total lignin content (Pettersen 1984). Linear regression of the hardwood data resulted in the equation

$$h_e = 7,774 + 27.4X_\ell \quad (4)$$

with an R^2 of 0.70. The standard errors are 40 for the estimate, 110 for the intercept, and 5 for the X_ℓ coefficient.

One sample of each of the four hardwoods was tested for acid-soluble lignin content to investigate its effect on the higher heating value. Acid-soluble lignin comprised 4.5, 5.8, 5.0, and 4.7% of oven-dry wood for maple, yellow-poplar, red oak, and basswood, respectively. Acid-soluble lignin thus comprised 17 to 22% of the total lignin content. A linear regression equation that increases the lignin content of the hardwoods by the corresponding acid-soluble lignin content for each species did not result in data more consistent with the softwood data.

DISCUSSION

The higher heating values of the extractive-free wood samples (Eqs. 2 to 4) reflect the higher heating value of lignin relative to cellulose and hemicellulose. Cellulose and hemicellulose have a higher heating value of 8,000 Btu/lb, whereas lignin has a higher heating value of 10,000 to 11,000 Btu/lb (Baker 1983). Using higher heating values of 7,527 Btu/lb for holocellulose and 11,479 Btu/lb for lignin, Tillman (1978) suggested that a reasonable formula for the higher heating value of wood is

$$h_o = 7,527C + 11,479(1 - C) \quad (5)$$

where

C = fraction holocellulose.

The equation assumes that the extratives have the same higher heating value as lignin. Rearranging Eq. (5) and assuming no extratives resulted in the equation

$$h_c = 7,527 + 39.52X_\ell \quad (6)$$

which is nearly identical to Eq. (3).

Extratives raised the higher heating values of the wood samples. In addition to higher lignin content, softwoods are considered to have greater higher heating values because of their resin or extractive contents. Chandler et al. (1983) reported the higher heating value as 7,720 calories per gram (13,896 Btu/lb). They also described terpenes and resin as the two classes of extratives that significantly affect the fire behavior of forest fuels. Howard (1973) calculated the higher heating value of resin as 15,000 to 16,000 Btu/lb. Although the percent extractive content improves the linear regression somewhat, it inadequately defines the effect of the extratives on the higher heating value of the different species. The residuals for Eq. (1) were greater for specimens with higher extractive contents. There are many different types of extratives and their higher heating values probably vary widely. Howard (1973) found that the alcohol/benzene extractive content of loblolly pine was positively correlated with the higher heating value ($R^2 = 0.54$).

Using 13,896 Btu/lb for the higher heating value of the extratives, Eq. (6) can be expanded to include the extractive content. The resulting equation is

$$h_o = 7,527 + 39.52\,X_\ell[(100 - X_E)/100] + 63.69X_E \quad (7)$$

Linear regression of my data results in the equation

$$h_o = 7,630 + 34.4\,X_\ell[(100 - X_E)/100] + 38.1X_E \quad (8)$$

where

$X_\ell[(100 - X_E)/100]$ = Klason lignin content (% oven-dry wood).

For Eq. (8), the R^2 *is 0.76.* The standard errors are 122 for the estimate, 113 for the intercept, 4 for the X_ℓ coefficient, and 10 for the X_E coefficient.

For a particular piece of wood, the appropriate coefficient for the last term of Eq. (7) would depend on the higher heating value of the extratives involved.

For the samples tested in this study, the mean difference in higher heating values of the softwoods and hardwoods was primarily caused by their difference in lignin contents. The average effect of the extratives was about the same for both the hardwoods and softwoods. However, species to species differences in higher heating values may be related more to the presence of extractives than to lignin content. The effect of extratives would have been greater if highly resinous samples had been tested. For example, the higher heating value of leaf pine materials with extractive contents of around 30% averages 10,600 Btu/lb (Howard 1973).

The higher heating values reported in this paper are expressed in terms of Klason lignin because Klason lignin values are widely reported. The higher heating value is directly related to the elemental composition of the wood. For fuels such as coal, the Dulong's formula (Perry and Chilton 1973) defines the higher heating value as a fraction of the carbon, hydrogen, oxygen, and sulfur contents. The heat content is related to the oxidation state of the natural fuels in which carbon atoms generally dominate and overshadow small variations of hydrogen content (Susott et al. 1975). Susott et al. (1975) found a linear relationship between the higher heating value and the carbon content of the natural fuels, chars, and volatiles. On the basis of literature values for different species of wood, Tillman (1978) also found a linear relationship between higher heating value and carbon content. The higher heating values for extratives, lignin, and holocellulose are consistent with their carbon content.

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