

CHEMICAL COMPOSITION AND THERMAL ANALYSIS OF COTTONWOOD

F. SHAFIZADEH AND G. D. MCGINNIS

Wood Chemistry Laboratory*, Department of Chemistry and School of Forestry, University of Montana, Missoula, Montana 59801 (U. S. A.)

(Received May 5th, 1970; accepted for publication, July 20th, 1970)

ABSTRACT

Analysis of extracted cottonwood shows the presence of lignin and 76.1% of cell-wall polysaccharides. The polysaccharides consist of cellulose (44.1%), 4-*O*-methylglucuronoxylan (20.8%), and glucomannan (9.7%). Differential thermal analysis and thermogravimetric analysis data show the relationship between the pyrolytic properties of the selected wood and its components.

INTRODUCTION

Understanding of the chemical reactions involved in pyrolysis and combustion of wood and wood products¹ provides a lead for coping with the problems of fire and solid-waste disposal which are significant factors for the safety and quality of the environment. Theoretically, dehydration and charring prevent the rapid flaming, combustion, and fragmentation, and volatilization provides a method for converting the residues into useful chemicals. However, this type of information is difficult to obtain directly with wood because of its chemical and physical inhomogeneity² and the complexity of the pyrolytic reaction of its components.

In this paper, the chemical composition of cottonwood and the pyrolytic properties of its components have been investigated as a systematic approach for analyzing pyrolysis and related properties of the original natural product.

Western cottonwood, *Populus trichocarpa*, which is selected as a low-grade hardwood, is found along the streams and rivers of the western United States. The chemical investigation of this species has been limited to certain commercial and biological aspects³⁻⁵ and to the phenyl glucosides found in the bark^{6,7}. Some information also has been available on the polysaccharides of the related species *Populus tremuloides* and *Populus grandidentata*⁸.

RESULTS AND DISCUSSION

A heartwood sample of the cottonwood was analyzed to provide the cell-wall polysaccharides and the other components shown in Table I.

*Established through a grant from the Hoerner-Waldorf Corporation of Montana.

TABLE I

COMPOSITION OF THE HEARTWOOD OF *Populus trichocarpa*

Component	Dry wood (%)	Extracted wood (%)
Benzene-alcohol (2:1) soluble	7.4	
Alcohol soluble	0.8	
TOTAL EXTRACTIVES		8.2
Klason lignin ^a		31.9 ^a
Cell-wall polysaccharides		76.1

^aIncludes acid decomposition products

Hydrolysis of the polysaccharides⁹ (holocellulose component) to the sugars listed in Table II indicated the presence of cellulose, "xylan", and "mannan". Isolation of the polysaccharides by the procedure of Jones and co-workers⁸ gave cellulose (42%), 4-*O*-methylglucuronoxylan (18%), and glucomannan (4.2%), based on the original wood substance.

TABLE II

ANALYSIS OF THE CELL-WALL POLYSACCHARIDES

Sugar	Holocellulose (%)
"Anhydro-D-glucose" units ^a	64.4
"Anhydro-D-xylose" units ^a	22.5
"Anhydro-D-mannose" units ^a	6.4
4- <i>O</i> -Methyl-D-glucuronic acid ^b	—
Acetyl group ^b	—

^aDetermined by analysis of the hydrolysis products. ^bBased on analysis of the functional groups.

The holocellulose fraction was also extracted with methyl sulfoxide to give a small yield of *O*-acetyl-4-*O*-methylglucuronoxylan¹⁰. This was used for the determination of acetyl groups, which are hydrolyzed under the alkaline condition of the systematic fractionation. Analysis of this product showed an acetyl content of 9.9%.

Hydrolysis of the "xylan" and analysis of the hydrolyzate showed the presence of D-xylose and only a trace of D-glucose. However, as usual, no 4-*O*-methyl-D-glucuronic acid was detected. The presence of this component was ascertained through methoxyl determination of 4-*O*-methylglucuronoxylan¹¹. This gave a value of 17.5% for the uronic acid residue in the acetylated "xylan". On the basis of these data, the *O*-acetyl-4-*O*-methylglucuronoxylan component contains an average of one uronic acid for each seven D-xylose residues, and approximately half of the D-xylose residues contain an acetyl group.

The glucomannan, on hydrolysis, provided D-glucose and D-mannose in the ratio of 1:1.

Assuming that, on hydrolysis of the cell-wall polysaccharides (see Table II), all the D-xylose is derived from *O*-acetyl-4-*O*-methylglucuronoxylan and the D-mannose is derived from the glucomannan fractions, the percentage of each polysaccharide may be calculated as shown in Table III. These data are in line with the general information available on hardwood xylans⁸ and the composition of the woods from arborescent angiosperms^{1,2}.

TABLE III

CELL-WALL POLYSACCHARIDES

Cell-wall polysaccharide	Holocellulose (%)		Wood (%)	
	Calc.	Isolated	Calc.	Isolated
Cellulose	58.0	54.7	44.1	41.6
4- <i>O</i> -Methylglucuronoxylan	27.3	23.7	20.8	18.0
Glucomannan	12.8	5.5	9.7	4.2

The thermal properties of cottonwood and its components were investigated by thermogravimetric analysis (t.g.a.) and differential thermal analysis (d.t.a.). The resulting thermograms are shown in Figs. 1 and 2. The t.g.a. curves (Fig. 1) indicate the rate of volatilization and the amount of residue left as the temperature is increased, whereas the d.t.a. curves show the exothermic and endothermic processes involved in the pyrolysis. Since Klason lignin is condensed and altered under the drastic treatment with acid, it was augmented with milled-wood lignin which is much closer to the native material¹³.

These data are further analyzed to show the nature of the chemical reactions which are involved in the pyrolysis of the individual polysaccharides and will be

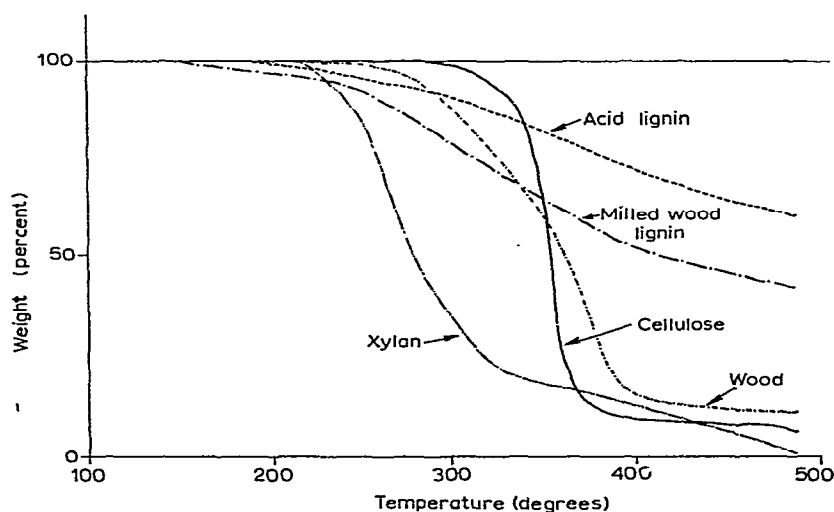


Fig. 1. Thermogravimetric analysis of cottonwood and its components.

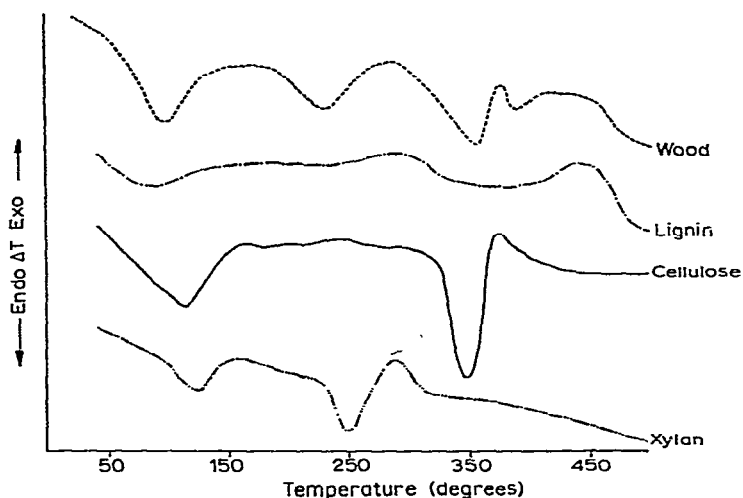


Fig. 2. Differential thermal analysis of cottonwood and its components.

reported elsewhere. However, it should be noted here that the thermograms of cottonwood reflect the thermal behavior of its major components, and the information that is obtained on these chemicals could be extrapolated, with confidence, to the original material. Furthermore, these data show that, under the experimental conditions (uncatalyzed reactions), lignin is the major source of char, whereas the carbohydrates are the precursors of the volatile products (tar and gases).

EXPERIMENTAL

Analysis of the ground wood. — A sample from heartwood of a healthy cottonwood tree was removed and ground in a Wiley mill to pass a 40-mesh screen. The ground wood was analyzed for the moisture content, extractives, and Klason lignin¹⁴ by standard methods. The extracted wood meal (81.9 g, dry weight) was delignified with acidic sodium chlorite^{15,16} to provide 62.3 g of holocellulose with 1.5% of residual lignin.

Isolation of hemicelluloses. — The procedure of Jones *et al.*⁸ was used for isolation of the hemicelluloses. The holocellulose fraction (84.8 g) was extracted with 24% aqueous potassium hydroxide. The extract was precipitated with acidic ethanol, dialyzed, and dried to provide 4-*O*-methylglucuronoxylan as a white powder (20.1 g; ash content, 0.15%), $[\alpha]_D^{25} - 78.3^\circ$ (*c* 2.6, 5% aqueous sodium hydroxide); lit.¹² $[\alpha]_D - 96$ to -61° .

The residue was extracted with 17.5% aqueous sodium hydroxide containing 4% of boric acid, and the extracted glucomannan was obtained as a white powder (4.7 g). The final residue was neutralized, washed, and dried to give cellulose (46.4 g).

Analysis of the polysaccharides. — The cell-wall polysaccharides were hydrolyzed, and the hydrolyzate was analyzed by g.l.c. by the method described by Laver

and co-workers⁹. The value for each sugar was corrected for the loss due to decomposition and addition of a water molecule during hydrolysis. The resulting data are given in Table II.

Similar analysis of the cellulose fraction gave only D-glucose, and the mannan component gave D-glucose and D-mannose in a ratio of 1:1.

Investigation of the "xylar." — The 4-O-methylglucuronoxylan fraction gave only D-xylose on hydrolysis. The percentage of 4-O-methyl-D-glucuronic acid residue (which is decomposed on hydrolysis) was determined from the methoxyl content (2.65%).

Direct extraction of the holocellulose (100 g) with methyl sulfoxide gave a small amount (10.0 g) of O-acetyl-4-O-methylglucuronoxylan (OAc, 9.87; OMe, 2.84%).

Dynamic thermal analysis. — The d.t.a. and t.g.a. data were obtained with a DuPont Model 900-950 thermal analyzer, programmed at the rate of 15°/min. The experiments were conducted in a nitrogen atmosphere by using silica beads as the reference and 5 mg of the ground wood or its components as the sample. For t.g.a. experiments, the gas flow was regulated at the rate of 100 ml/min.

ACKNOWLEDGMENT

The authors thank the U. S. Forest Service and Northern Forest Fire Laboratory for their interest and support of this work through cooperative agreement 12-11-204-1, supplement No. 17.

REFERENCES

- 1 F. SHAFIZADEH, *Advan. Carbohydr. Chem.*, 23 (1968) 919.
- 2 F. SHAFIZADEH AND W. J. NEARIN, *Mater. Res. Std.*, 6 (1966) 593.
- 3 K. MEHRING AND W. SCHRAMM, *Tierzucht.*, 1 (1949) 11.
- 4 H. BUTIN, *Ber. Deut. Botan. Ges.*, 73 (1960) 185.
- 5 L. MOZEIKA AND V. SERGEEVA, *Izv. Akad. Nauk Latv. SSR*, 12 (1957) 217.
- 6 V. LOESCHKE AND H. FRANCKSEN, *Naturwissenschaften*, 51 (1964) 140.
- 7 I. A. PEARL AND K. LARSON, *Tappi*, 48 (1965) 714.
- 8 J. K. N. JONES, C. B. PURVES, AND T. E. TIMELL, *Can. J. Chem.*, 39 (1961) 1059; J. O. THOMPSON AND L. E. WISE, *Tappi*, 35 (1952) 331.
- 9 M. L. LAVER, D. F. ROOT, F. SHAFIZADEH, AND J. C. LOWE, *Tappi*, 50 (1967) 618.
- 10 E. HÄGGLUNG, B. LINDBERG, AND J. MCPHERSON, *Acta Chem. Scand.*, 10 (1956) 1160.
- 11 R. J. ROSS AND N. S. THOMPSON, *Tappi*, 48 (1965) 376.
- 12 T. E. TIMELL, *Advan. Carbohydr. Chem.*, 19 (1964) 297.
- 13 B. L. BROWNING (Ed.), *The Chemistry of Wood*, Interscience, New York, London, 1963.
- 14 *ASTM, Standards on Wood, Wood Preservatives, and Related Materials*, Preparation of Extractive-free Wood, D1105-56, Lignin in Wood, D1106-56, Philadelphia, 1954.
- 15 T. E. TIMELL, *Methods Carbohydr. Chem.*, 5 (1963) 134.
- 16 L. E. WISE, in L. E. WISE AND B. C. JAHN (Eds.), *Wood Chemistry*, Vol. 2, Reinhold, New York, 1952, p. 1145.