

Saccharification of Douglas-Fir Wood by a Combination of Prehydrolysis and Pyrolysis

FRED SHAFIZADEH and THOMAS T. STEVENSON, *Wood Chemistry Laboratory, Department of Chemistry, University of Montana, Missoula, Montana 59812*

Synopsis

A process has been investigated for the saccharification of wood, involving prehydrolysis, lignocellulose pyrolysis, and tar hydrolysis. In this process, ground wood was first prehydrolyzed to remove the more readily hydrolyzable hemicelluloses. The residual lignocellulose was then pyrolyzed rapidly to provide a tar containing levoglucosan and its condensation products. The tar was hydrolyzed to convert these products to glucose. Laboratory experiments have shown that this process can convert a common softwood such as Douglas-fir to 14% char and 42% hexoses. This amounts to a 59% recovery of the hexoses: 32% from prehydrolysis and 27% from pyrolysis. The prehydrolysis served not only to remove hemicelluloses, but also to increase the yield of glucose from pyrolysis and subsequent tar hydrolysis. It has been shown that this enhancement is due to the removal of inorganic ash and the catalytic effect of trace amounts of acid remaining in the lignocellulose.

INTRODUCTION

Saccharification of wood represents a major step in the utilization of biomass by chemical conversion. Traditionally this has been achieved by acid hydrolysis through several processes which are well known and have been extensively investigated.¹ These processes require high temperature and pressure, or a high acid concentration. Therefore, despite various developments, they have not been extensively developed as industrial processes. In recent years considerable attention has been focused on enzymatic hydrolysis, which proceeds under much milder conditions but also at a slower rate and for practical purposes requires some modification or pretreatment of the substrate.² Another alternative is pyrolytic depolymerization. This process takes place much faster than the others, but is less specific and normally provides a very low yield from wood and the commonly available cellulosic materials.^{3,4} Therefore, it has not received sufficient attention.

In this article we describe a pyrolytic method for saccharification of Douglas fir, as a commonly available softwood. This method is based on previous results obtained in this laboratory⁴ and the well known fact that the hemicellulose components of wood can be removed readily by prehydrolysis.

EXPERIMENTAL

A sample of Douglas fir (*Pseudotsuga menziesii*, Rocky Mountain form) was obtained locally, and the heartwood carefully separated from the bark and sapwood. The heartwood was then ground in a Wiley Mill, sieved to 20/60 mesh, and air-dried. Organic extractives were removed by extraction in a Soxhlet

extractor with chloroform for 8 h and then with toluene-ethanol (1:2) for 8 h and finally three 1-h washes with boiling water.

Prehydrolysis of extracted wood was performed in one of two ways; either on a 1 g scale with 18 mL of 0.1M sulfuric acid in a 20-mL sealed glass ampoule immersed in an isothermal oil bath heated at 115°C, 130°C, 145°C, 160°C, or 175°C for 1 h or on a 50-g scale with 1 L of 0.5M sulfuric acid solution in a Parr Model 4501 pressure reaction apparatus equipped with an internal stirrer and cooling coils, for 1 h at 130°C. Large scale prehydrolysis provided a bulk sample of lignocellulose used as the substrate for the data shown in Figure 3, while small scale prehydrolysis was used for other quantitative experiments. The resulting lignocellulose was then separated from the acid-sugar solution by filtration on sintered glass and washed with distilled water.

The acid-sugar solution and washings were diluted to a known volume, and an aliquot was neutralized with solid BaCO₃ and centrifuged. This solution was quantitatively analyzed for arabinose, xylose, mannose, glucose, and galactose by gas chromatography of the aldononitrile acetates, using glucitol as an internal standard.⁵

Cellulosic samples were pyrolyzed in a tube furnace, as described previously.^{6,7} All pyrolyses were for 5 min, at 400°C, under vacuum (1.5 torr of nitrogen), and the furnace was tipped at an angle of ~10° to allow the condensed tar to flow more easily from the furnace, thus reducing secondary decomposition. The tar was then washed from the inner collection tube with methanol and dried *in vacuo* at 45°C, weighed, and redissolved in methanol. A small aliquot was removed, acetylated, and analyzed for levoglucosan by gas chromatography in the same manner used for sugar analysis.⁵

An aliquot of the tar solution was then removed for hydrolysis. Hydrolysis was performed on 1/10–1/20 of the total tar with 1 mL of 0.05M H₂SO₄ in a sealed 5-mL glass ampoule placed in a 130°C oil bath for 1 h. The acid-sugar solution was then carefully washed into a flask containing the internal standard, neutralized, and analyzed as described above.

Ash contents were determined gravimetrically on a 25-mg scale, by heating in an oxygen atmosphere for 3 h, in a furnace programmed from 250°C to 400°C at 8°/min. The weight of the remaining residue was expressed as a percentage of the dry weight of the original substrate.

Acid-washed substrates were prepared by stirring in 0.1M H₂SO₄ at room temperature for 3 h, followed by washing with distilled water in a Soxhlet extractor for 8 h, and drying at 50°C, *in vacuo*. Sulfuric acid was added to substrates as a methanolic solution. The methanol was then removed at 40°C, *in vacuo*, in a rapidly rotating flask, to give the desired concentration.

Holocellulose was prepared by a modification of the chlorite method,⁸ involving delignification over a period of 260 min. The sugar contents of wood and lignocellulose were analyzed by hydrolysis with trifluoroacetic acid,⁹ followed by GC analysis.⁵ The Klason lignin content was determined by sulfuric acid hydrolysis.¹⁰ Numerical results were rounded to the nearest percentage.

RESULTS AND DISCUSSION

In order to provide a homogeneous substrate, ground, extracted Douglas-fir heartwood was chosen as a representative sample of a softwood. It was found to contain 1% arabinan, 6% xylan, 16% mannan, 48% glucan and galactan, 27%

Klason lignin, and 0.1% ash, or an overall content of 7% pentosans and 64% hexosans.

An overview of the process is shown in Figure 1. The yields resulting from this procedure can be expressed in two ways, either based on the original weight of the wood (wt %) or based on the number of hexose (or pentose) residues in the ground wood (mol %). Both ways are used in this paper. The extracted wood (0.88 g) was prehydrolyzed in 0.1M sulfuric acid at 160°C for 1 h to provide 65% lignocellulose (0.57 g) and 29% reducing sugars (0.255 g, wt %), including 5% pentoses (0.045 g) and 24% hexoses (0.21 g). This represents 67% of the pentose content, 34% of the hexose content, and 37% of the total carbohydrates in the wood (mol %). Since the pentoses are more subject to degradation during hydrolysis and their amount in softwood is very little (~7%), the yields of the pentoses expressed as a percentage of the total pentose content are not very meaningful and fluctuate between 45% and 70% (3–5 wt %). The insoluble lignocellulose was then washed with distilled water on a Gooch crucible, and a portion (0.44 g) was

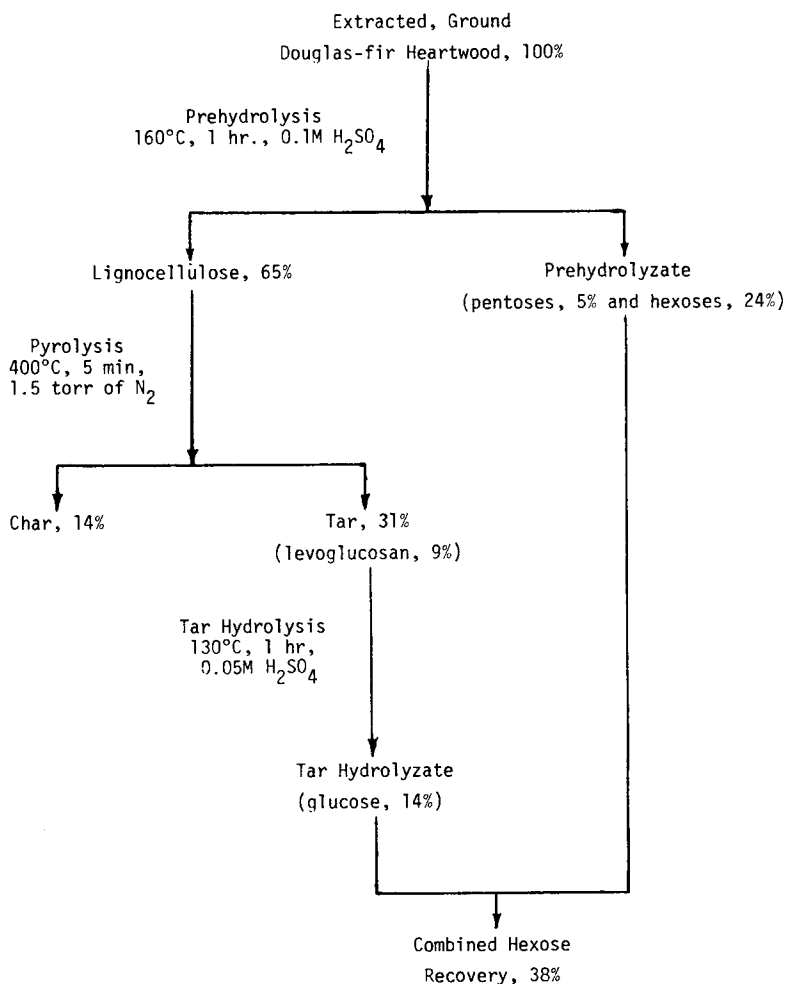


Fig. 1. Saccharification of Douglas-fir heartwood by prehydrolysis, pyrolysis, and tar hydrolysis. Percentages are wt %.

pyrolyzed. This gave 31% tar (0.21 g) containing 9% levoglucosan (1,6-anhydro- β -D-glucopyranose, 0.061 g) and an aliquot of the tar (0.21 g) was hydrolyzed to give 14% glucose (0.0095 g, wt %). In the entire procedure 67% of the pentoses and 54% of the hexoses in the wood were recovered as free sugars (mol %).

The temperature of prehydrolysis can affect the efficiency of the process, as shown in Table I. At temperatures below 130°C, sugar yields obtained from the prehydrolysis were low, due to incomplete hydrolysis of the hemicelluloses, which are then only partially recovered by the less efficient pyrolytic step. At temperatures above 160°C, the yield of hexoses was higher than expected from the hemicellulose component. Furthermore, this increase was entirely due to glucose, indicating the onset of cellulose hydrolysis. This increase, however, was accompanied by an increase in sugar degradation (which is particularly apparent from the pentose yield) and led to a reduced amount of lignocellulose. On this basis a prehydrolysis temperature of 160°C was chosen for most future experiments as the optimum condition (see Table I). However, it should be noted that the overall hexose yields are not significantly different within the prehydrolysis temperature range of 130–175°C.

Pyrolyses were carried out under vacuum at 400°C. Previous kinetic studies with cellulose have shown at this temperature pyrolysis proceeds very rapidly and still provides good yields of tar and levoglucosan.^{4,6} The tar contains some levoglucosan and its condensation products, both of which hydrolyze to glucose.¹¹ Therefore, the amount of free sugar obtained from the hydrolysis of the tar is more than what would be expected from the hydrolysis of levoglucosan alone.

This constitutes one of the attractive features of this process. Possible options for utilizing this tar include separating the levoglucosan from the tar by crystallization and using it as an anhydro-sugar, or hydrolyzing the tar to glucose for fermentation to alcohol or other applications. Since isolation of levoglucosan from the tar by crystallization is a relatively difficult and low yield process and does not utilize the condensation products of levoglucosan, the latter alternative may be preferred. Another attractive feature is that the tar can be hydrolyzed by addition to the acidic prehydrolysis liquors, and the resulting glucose used along with the other hexoses (mannose, galactose, and glucose), obtained from the prehydrolysis. This avoids the necessity of separate neutralization and processing of the fermentable sugars.

Tar was hydrolyzed under milder conditions than were hemicelluloses. Figure 2 shows the yield of glucose from an aliquot of tar as a function of hydrolysis time in 0.05M sulfuric acid at 130°C. Gas chromatographic analysis showed that,

TABLE I
Effect of Prehydrolysis^a Temperature on Product Yields^b

Temp (°C)	Prehydrolysis products (%)			Hexose from tar hydrolysis (%)
	Pentoses	Hexoses	Lignocellulose	
115	3	7	82	10
130	5	18	75	16
145	5	19	70	16
160	5	24	65	14
175	0.4	27	47	8

^a 0.1M H₂SO₄ for 1 h.

^b Expressed as wt % of wood.

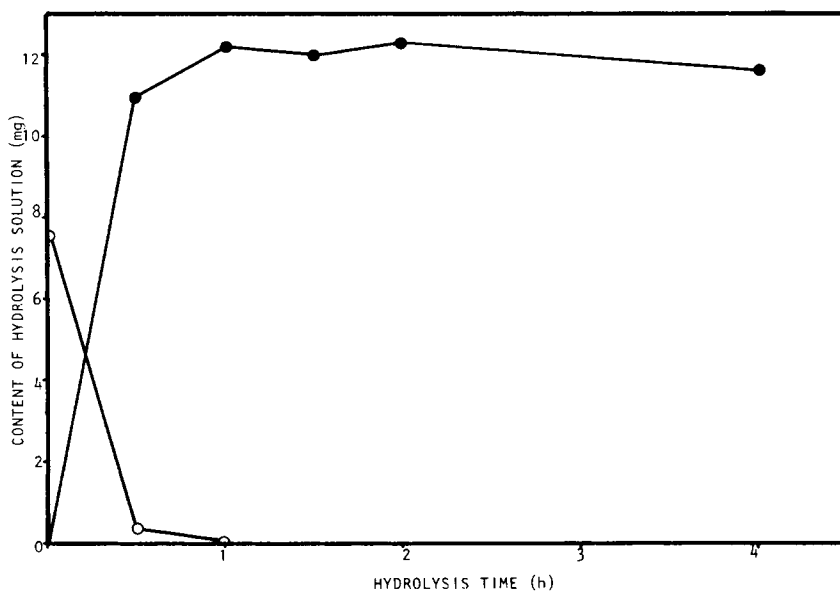


Fig. 2. Hydrolysis of tar in 0.05M H_2SO_4 at 130°C, obtained from the pyrolysis of Douglas-fir lignocellulose: (●) glucose; (○) levoglucosan.

after 0.5 h, the maximum yield of glucose had almost been obtained, but that a small amount of levoglucosan still remained. After 1 h, hydrolysis was complete. Further tar hydrolyses were routinely carried out in 0.05M sulfuric acid, 130°C, for 1 h. These data show that the conditions required for prehydrolysis and tar hydrolysis are both much less drastic than those required for cellulose hydrolysis.

Previous studies have shown that different types of cellulose and cellulosic materials that have a history of acid treatment provide better yields of tar and 1,6-anhydro-sugars upon pyrolysis.^{4,12,13} This includes acid-washed cotton, Whatman CF-11 cellulose powder, wood, wood-derived substrates, and mannan. These data are particularly interesting because it is known that Arrhenius and Lewis acids catalyze dehydration of cellulose and levoglucosan to unsaturated sugars and enhance the charring process.¹⁴

In this study a small amount of sulfuric acid added to Douglas-fir lignocellulose, as a catalyst prior to pyrolysis, increased both tar and levoglucosan yields (Fig. 3). However, the amount of acid was critical. The addition of trace amounts of acid (up to 0.01%) had very little effect, while the addition of 0.1% sulfuric acid doubled the yield of levoglucosan. When the acid concentration was further increased to 1.0%, the yields dropped back to the uncatalyzed level.

To determine the yields that could be obtained and the effect of small amounts of sulfuric acid, the process was carried out with and without acid added to lignocellulose that had been carefully extracted with water for 8 h in a Soxhlet extractor (Table II). Without the addition of acid to the lignocellulose, 22% of the wood was recovered as free hexoses from the prehydrolysis, and 10% from the tar hydrolysis, amounting to an overall yield of 45% of the hexose content in the wood. When 0.1% acid was added back to the lignocellulose, the recovery of hexoses following tar hydrolysis was 19%, and this increased the overall hexose yield to 59%.

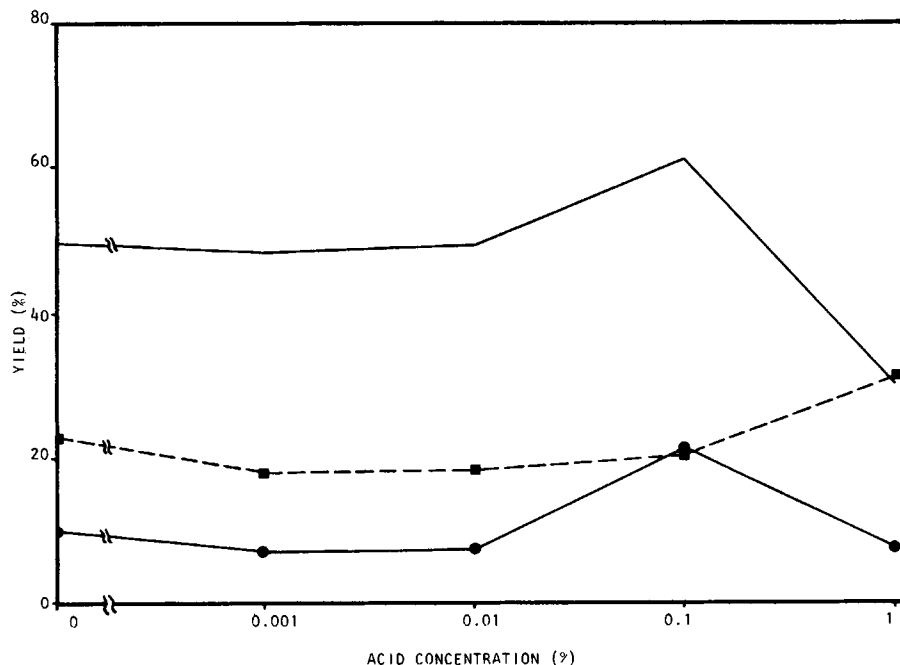


Fig. 3. Product yields from Douglas-fir lignocellulose pyrolysis, expressed as % of the lignocellulose: (no symbol) tar; (■) char, (●) levoglucosan.

To further investigate the acid enhancement, other cellulosic substrates were treated with acid. The results summarized in Table III are as follows. The addition of 0.1% sulfuric acid to purified cellulose (CF-11) caused no change in the tar yield and led to a small decrease in the levoglucosan yield. Apparently, acid concentration is critical as shown by the addition of different amounts of ammonium sulfate to cotton cellulose which resulted in an increase or decrease in levoglucosan yield¹⁵ according to the concentration. Holocellulose prepared from Douglas-fir heartwood had a very high ash content and a very low levoglucosan yield, and showed no improvement by the addition of acid. Acid washing, however, removed a large portion of the ash and resulted in a greatly increased levoglucosan yield, but the addition of acid gave no further enhancement. Lignocellulose had a low ash content, due to the acid prehydrolysis, and, as seen previously, the addition of acid resulted in a twofold increase in levoglucosan yield. Extracted and carefully water-washed Douglas-fir heartwood gave only 7% levoglucosan upon pyrolysis, and, when acid was present, the levoglucosan yield was doubled. Acid washing of this substrate lowered the ash content significantly. However, this was accompanied by only a small increase in levoglucosan yield, possibly because the ash content was low prior to the acid wash and only marginally affected levoglucosan formation.

The enhancement in levoglucosan formation following acid washing could be due to the removal of inorganic impurities or the addition of trace amounts of acid that catalyze the transglycosylation reaction. The former is most likely however, since, in these experiments, acid was rigorously removed by 8 h of extraction with water and, also, since acid washing appears to be most effective when a large amount of inorganic material is present in the substrate.

TABLE II
The Effect of 0.1% Sulfuric Acid on Product Yields^a

Pentoses	Prehydrolysis products (%) ^b		Acid added to lignocellulose ^c	Pyrolysis products (%)		Tar hydrolysis glucose (%) ^d	Total hexoses
	Hexoses	Lignocellulose		Tar	Levogluconan		
3.5	22	63	no	27	6	10	32
4	22	63	yes	34	15	19	42

^a All yields expressed as a wt % of wood.

^b Prehydrolysis conditions: 160°C, 1 h, 0.1M H₂SO₄.

^c Lignocellulose was Soxhlet-extracted with water.

^d Tar hydrolysis conditions: 130°C, 1 h, 0.05M H₂SO₄.

TABLE III
Product Yields from the Pyrolysis of Various Cellulosic Substrates

Substrate	Washing	Ash	Char	Tar	Levoglucosan
CF-11	Acid		5	68	36
CF-11 + H ₂ SO ₄ ^a	Acid		7	63	35
Holocellulose	None	0.6	17	26	1
Holocell + H ₂ SO ₄	None	0.6	17	27	1
Holocellulose	Acid	0.05	8	66	26
Holocell + H ₂ SO ₄	Acid	0.05	9	57	23
Lignocellulose	Water	<0.02	24	44	12
Lignocell + H ₂ SO ₄	Water	<0.02	24	51	26
Wood	Water	0.1	17	45	7
Wood + H ₂ SO ₄	Water	0.1	17	48	14
Wood	Acid	<0.02	16	51	9
Wood + H ₂ SO ₄	Acid	<0.02	17	50	19

^a All H₂SO₄ added as 0.1% of substrate.

Under the conditions employed in these experiments, the addition of small amounts of acid appeared to be most effective when lignin was present. The mechanism of this phenomenon, however, is not clear and cannot be simply attributed to cleavage of the lignin-carbohydrate bonds, because these bonds are known to break under the prehydrolysis conditions.

CONCLUSIONS

The combination of acid hydrolysis and pyrolysis provides a unique method for the saccharification of wood and biomass in general. In this process the hemicelluloses which are more amenable to hydrolysis are removed by a relatively mild prehydrolysis, and the remaining lignocellulose is pyrolyzed to a tar and a char residue. The tar contains levoglucosan as well as its condensation products, all of which are easily hydrolyzable to glucose. When the process is carried out with a softwood such as Douglas fir, in which the principal hemicelluloses are glucomannans and galactoglucomannans, the prehydrolyzate contains mainly hexoses. Addition of the pyrolysis tar to this mixture before neutralization increases the concentration of the hexoses that could be used for fermentation. The residual char could be used as fuel. Based on laboratory experiments this process provided a 59% recovery of the hexoses (37% of the wood) and 14% char. This is a much better yield than what may be reasonably expected from the direct pyrolysis of wood, since under normal conditions this provided 45% tar containing only 7% levoglucosan.

It has been shown that an acid wash increases the yield of levoglucosan by removal of inorganic materials before pyrolysis. Also, trace amounts of acid increase levoglucosan yields from the lignified material. In this process these effects are combined with the removal of easily hydrolyzable, noncellulose polysaccharides by prehydrolysis, rapid depolymerization of the cellulose by pyrolysis, recovery of free sugars from both levoglucosan and its condensation products in the tar, and, finally, the possibility of using the acidic prehydrolysis liquors for the tar hydrolysis before neutralization to gain processing economy and efficiency in wood saccharification.

For these experiments, the heartwood was separated from the sapwood,

ground, and extracted. This provided a homogeneous substrate suitable for small-scale laboratory experiments. Grinding is important in order to allow rapid penetration of acid during prehydrolysis and escape of volatiles during pyrolysis. However, the saccharification of sapwood would be expected to give results similar to those from heartwood, since they contain the same lignocellulose and hemicellulose components. The effects of extractives on prehydrolysis and pyrolysis have not been studied but are not expected to be significant. Thus, while grinding is important, the separation of heartwood and sapwood is not essential for the recovery of hexoses.

The authors are pleased to acknowledge the support of the National Science Foundation, Research Grant No. PFR80-23854, Professor G. N. Richards for helpful discussions, and E. W. Bowling and M. T. Larkin for technical assistance.

References

1. M. Oshima, *Wood Chemistry Process Engineering Aspects*, Noye Development Corp., New York, 1965.
2. R. D. Brown and L. Jurasek, *Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid Catalysis*, R. D. Brown and L. Jurasek, Eds., American Chemical Society, Washington, D.C., 1979.
3. F. Shafizadeh, *Appl. Polym. Symp.*, **28**, 153 (1975).
4. F. Shafizadeh, R. H. Furneaux, T. G. Cochran, J. P. Scholl, and Y. Sakai, *J. Appl. Polym. Sci.*, **23**, 3525 (1979).
5. C. C. Chen and G. D. McGinnis, *Carbohydr. Res.*, **90**, 127 (1981).
6. A. G. W. Bradbury, Y. Sakai, and F. Shafizadeh, *J. Appl. Polym. Sci.*, **23**, 3271 (1979).
7. F. Shafizadeh, R. H. Furneaux, T. T. Stevenson, and T. G. Cochran, *Carbohydr. Res.*, **61**, 519 (1978).
8. B. L. Browning, *Methods of Wood Chemistry*, Vol. II, Interscience, New York, 1967, p. 395.
9. D. Fengel and G. Wegener, in Ref. 2, pp. 145-158.
10. American Society for Testing and Materials, *Annual Book of ASTM Standards*, ASTM, Philadelphia, 1972, part 16, pp. 373-374, Designation: D1106-56.
11. F. Shafizadeh and Y. L. Fu, *Carbohydr. Res.*, **29**, 113 (1973).
12. R. H. Furneaux and F. Shafizadeh, *Carbohydr. Res.*, **74**, 354 (1979).
13. H. J. P. Venn, *J. Textile Inst.*, **15**, T414 (1924).
14. F. Shafizadeh, Y. Z. Lai, and C. R. McIntyre, *J. Appl. Polym. Sci.*, **22**, 1183 (1978).
15. A. Basch and M. Lewin, *Textile Res. J.*, **43**, 693 (1973).

Received February 2, 1982

Accepted June 11, 1982