

# Production of Levoglucosan and Glucose from Pyrolysis of Cellulosic Materials

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## Synopsis

Vacuum pyrolysis of cellulose within the temperature range of 300–500°C provides a tar fraction containing mainly levoglucosan and glucose condensation products. It was found that pyrolysis proceeds at a much faster rate at the higher temperatures without detrimental effect on the yields. At 400°C the reaction was essentially complete within 3 min yielding a tar that contained 39% levoglucosan and, upon mild acid hydrolysis, gave 49% D-glucose. The yields could be further improved by washing or treatment of cellulosic substrates with acids. Cotton hydrocellulose provided up to 58% levoglucosan or 77% D-glucose. This is the highest yield determined by unequivocal methods. Commonly available cellulosic materials such as wood and newsprint give very poor yields of levoglucosan. However, the yields could be improved substantially by acid washing or prehydrolysis to the extent that pyrolysis of these substrates may become an attractive industrial process. The data in this report provide the technical basis for such a process and resolve the existing controversies on the reported yields.

## INTRODUCTION

Current efforts for development of alternative sources of energy and chemical feedstock have focused considerable interest on more intensive utilization of renewable cellulosic materials. These materials can be converted to glucose and sugar derivatives by acidic, enzymic, and pyrolytic methods. However, commercial applications are hampered by economic considerations. Acid hydrolysis is slow and cumbersome, while enzymic hydrolysis requires costly pretreatment to increase the accessibility and susceptibility of the substrate. Pyrolytic depolymerization is hampered by a lack of specificity; however, this process deserves special consideration because of its inherent efficiency and compatibility with modern engineering technology including fluidized bed processes.

Pyrolysis of cellulose to levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) was reported 60 years ago by Pictet and Sarasin.<sup>1</sup> However, the yield of levoglucosan that could be obtained from pure cellulose was indefinite and controversial.<sup>2–5</sup> Pyrolyzates from commonly available cellulosic materials such as paper and wood contained very little levoglucosan<sup>6–9</sup> and were better suited for fuel rather than chemical feedstock for sugar derivatives. Furthermore, reliable kinetic data were missing to indicate the optimal pyrolytic conditions.

Detailed studies at this laboratory to unravel the pyrolytic reactions<sup>3,10–15</sup> indicated that at temperatures above 300°C, the glycosidic bond in cellulose is substituted by one of the free hydroxyl groups. This intramolecular transglycosylation provides anhydrosugars which are subsequently interconverted and

partially repolymerized by intermolecular transglycosylation to provide a tarry mixture of levoglucosan, its furanose isomer (1,6-anhydro- $\beta$ -D-glucofuranose), and randomly linked oligo- and polysaccharides.<sup>10</sup> The tar fraction also contains a variety of minor products resulting from competing dehydration, elimination, and disproportionation reactions. The latter decomposition reactions predominate at lower temperatures.<sup>11,13</sup> The tar fraction could be hydrolyzed under mild conditions to give a relatively high yield of glucose. In addition, there are other more volatile compounds, gaseous fission products, and a charred residue that could be collected as separate fractions.

In the light of these experimental findings, a review of the literature reveals that reported yields of levoglucosan greater than 50% are overestimates. Golova and co-workers<sup>4,16-18</sup> determined levoglucosan as the increased reducing sugar content of the tar after hydrolysis and reported yields up to 63%. More recently, other Russian workers<sup>19,20</sup> used the same procedure in estimating 25% and 36% yields of levoglucosan from pyrolysis of lignocellulose and cellulose respectively. However, in addition to levoglucosan, other tar constituents such as 1,6-anhydro- $\beta$ -D-glucofuranose, oligo- and polysaccharides which hydrolyze to D-glucose, and 1:4,3:6-dianhydro- $\alpha$ -D-glucopyranose,<sup>12,21</sup> which hydrolyzes to 3,6-anhydro-D-glucose, will account for a large portion (up to 30% based on cellulose<sup>10</sup>) of these reducing sugar values. Sandermann and Augustin,<sup>22</sup> who reported a 73% yield of levoglucosan from cellulose, fractionated the pyrolysis tar by paper chromatography, then determined levoglucosan by a nonspecific phenol-sulfuric acid colorimetric method. The chromatographic levoglucosan fraction, however, almost certainly contained 1,6-anhydro- $\beta$ -D-glucofuranose, and the overall analysis procedure was subject to considerable experimental error. Using the same analytical procedure, Kosik and Reiser<sup>9</sup> more recently estimated a 62% yield of levoglucosan from cellulose. An unreliable quantitative infrared analysis procedure led Holmes and co-workers<sup>23</sup> to report a 63% yield of levoglucosan, but this method was later modified, and a lower maximum yield of 44% was confirmed by trimethylsilylation and gas-liquid chromatographic (GLC) analysis.<sup>24</sup> On other occasions,<sup>25,26</sup> the tar has been equated with levoglucosan on the mistaken assumption that the two are virtually identical. An early analysis technique<sup>27</sup> involved the isolation of the tribenzoate derivative of levoglucosan from cellulose pyrolyzates, but this procedure gave low estimates of the levoglucosan present.

Reported yields of levoglucosan determined by trimethylsilylation and GLC procedures are considered to be reliable.<sup>10,21,24,28,29</sup> However, in these cases the maximum yields of levoglucosan from pyrolysis of cellulose ranged between 22% and 48%.

This article describes the results obtained in our laboratory on improvements in the yields of levoglucosan, D-glucose, and tar from pyrolysis of various cellulosic substrates using controlled pyrolytic and pretreatment techniques. These data resolve many of the existing controversies on the reported yields and could be used for designing commercial processes for production of levoglucosan and/or glucose. Levoglucosan as such may be useful as an industrial polyol,<sup>30,31</sup> and the D-glucose solution may be fermented to ethanol, used as a nutrient for protein production, or converted to other industrial products.

## EXPERIMENTAL

### Materials and Pretreatments

The following cellulose samples were obtained commercially: Whatman CF 11 powder (max. ash 0.015%), Whatman No. 41 ashless filter paper (max. ash 0.01%), Whatman No. 1 filter paper (0.06% ash), Avicel microcrystalline (0.004% ash, FMC Corp.), and Baker TLC microcrystalline (max. ash 0.05%, J. T. Baker Chem. Co.). Cotton linters and cotton fabric were obtained from the Southern Regional Research Laboratory, USDA, New Orleans. The linters had been scoured with 2% sodium hydroxide for 1 hr, and were washed with boiling ethanol and then water at 80°C as reported previously.<sup>12</sup> The fabric had been desized, scoured, and bleached under mild conditions. Cotton hydrocellulose was prepared from cotton linters in boiling hydrochloric acid (constant-boiling mixture) for 3 min<sup>32</sup> and was washed to neutrality with distilled water. Newsprint samples consisted of daily newspaper containing black ink, and kraft paper samples were obtained from commercial shopping bags. The cloth and paper samples were cut into approx. 7 × 60 mm<sup>2</sup> strips or where stated ground to 40 mesh in a Wiley mill. Cottonwood, supplied by the Northern Forest Fire Laboratory, Missoula, was ground to 20–60 mesh in a Wiley mill, extracted with diethyl ether and benzene–ethanol (2:1) in a Soxhlet extractor, washed with water at 50°C, and dried at 80°C.

Cottonwood lignocellulose was prepared by heating cottonwood with 10 times its weight of 1% sulfuric acid in a Parr Model 4501 pressure reaction apparatus at 160°C for 1 hr, washing the product with distilled water to neutrality, and drying it at 80°C. Cottonwood holocellulose was prepared from the same cottonwood by a standard sodium chlorite–acetic acid delignification procedure<sup>33</sup> adapted to give a total reaction time of 1.75 hr.

Washing pretreatments of cellulosic samples in dilute acid or base were conducted at room temperature with stirring or occasional agitation for about 2 hr. After each treatment the samples were thoroughly washed with distilled water to neutrality.

All yields reported in this paper are based on the dry weight of the pyrolysis substrate, the moisture contents of which were determined by oven drying samples at 120–125°C for 30 min. Ash contents were determined by Galbraith Laboratories, Knoxville, Tennessee.

### Pyrolysis Conditions

Samples (0.5 g) were pyrolyzed in a tube furnace as previously reported.<sup>13,34</sup> The tar, which during vacuum pyrolysis condensed at the edge of the heated zone, was washed from the inner collection tube with methanol. This procedure left a small methanol-insoluble residue in the tube. For analysis of D-glucose, this residue was recovered with water and added to the tar solution before hydrolysis.

For pyrolysis at atmospheric pressure, the pyrolysis tube was swept with a 200 ml/min nitrogen flow. Since the tar partly condensed within the heated zone, the pyrolysis procedure was modified by holding the sample boat in the furnace with a rigid wire and moving the inner collection tube out through the condenser as the pyrolysis progressed. This greatly reduced secondary decomposition of the tar.

The tar weight was determined by evaporating the solution in vacuo and then either allowing the residue to equilibrate to constant weight under atmospheric conditions (method A) or to dry in vacuo over phosphorous pentoxide (method B). The char remaining in the boat was cooled to room temperature and weighed.

### Analysis for Levoglucosan

An aliquot of the tar solution was evaporated to dryness in vacuo and analyzed for levoglucosan and 1,6-anhydro- $\beta$ -D-glucofuranose content by trimethylsilylation and GLC as previously reported.<sup>34</sup> The following modifications were made during the course of this work: the stainless steel GLC column was replaced by a nickel column, and methyl arachidate was substituted for *myo*-inositol as internal standard. Levoglucosan yields were calculated as wt. % of the pyrolysis substrate.

### Tar Hydrolysis and Glucose Analysis

An aliquot of the tar was hydrolyzed in 1*N* sulfuric acid (25 ml) heated in a boiling water bath at 97°C for 4 hr and was then diluted to 50 ml. An aliquot (9 ml) of this was mixed with 1 ml *myo*-inositol solution (8–12 mg/ml, GLC internal standard), and the resulting solution was neutralized with anion exchange resin (Amberlite IR-45). An aliquot (1 ml) of this solution was evaporated to dryness and analyzed for D-glucose, determined as the sum of  $\alpha$ - and  $\beta$ -anomers, by trimethylsilylation and GLC. GLC was performed on a nickel column (1.8 m  $\times$  2.2 mm I.D.) packed with 3% SE-30 on 80–100 mesh Gas-Chrom Q, programmed from 75 to 225°C at 10°C/min. To ensure complete silylation of the inositol, samples being derivatized were placed in an ultrasonic bath for 0.5 hr.

### Reducing Sugar Determinations

The reducing sugar value of the tar, calculated as D-glucose, was determined by the Somogyi method.<sup>35</sup> This value represents the weight, in mg, of glucose which produces the same reducing value as 100-mg tar. It corresponds to reducing power and not specifically to glucose content. Hydrolysis was conducted by mixing an aqueous aliquot of tar solution with an equal volume of 2*N* sulfuric acid, heating in a boiling water bath at 97°C for 4 hr, and neutralizing with dilute sodium hydroxide to a phenolphthalein endpoint.

### Thermal Analysis

DTG (derivative thermogravimetry) and DTA (differential thermal analysis) data were obtained using 2-mg samples heated in open aluminum pans at 15°C/min in a 75 ml/min nitrogen flow at atmospheric pressure as previously reported.<sup>36</sup>

## RESULTS AND DISCUSSION

## Effects of Pyrolysis Conditions

Since pyrolysis of cellulose provides levoglucosan in addition to a variety of other glucose derivatives, the proposed scheme for pyrolytic utilization of cellulosic materials involves isolation of levoglucosan as a crystalline compound and subsequent hydrolysis of the remaining tar to glucose or, alternatively, hydrolysis of the entire tar fraction to glucose.

Figure 1 shows the extent of hydrolysis of a typical tar fraction as monitored by reducing sugar determination. The required conditions for this reaction (5% sulfuric acid at 97°C for 2 hr) are much milder than those required for hydrolysis of cellulose.<sup>37,38</sup> Thus, the pyrolysis method could be augmented by a mild hydrolysis step to obtain a much higher yield of usable products.

For this study, Whatman CF 11 powder was chosen as a standard cellulose substrate to investigate the possibilities for increasing yields by controlled pyrolysis and for defining the optimum conditions. The rate of production of tar and char on pyrolysis of this substrate under vacuum, as a function of oven temperature was monitored at 25°C intervals from 300 to 500°C. The results shown in Figures 2 and 3 indicate that above 400°C pyrolysis is essentially complete within 3 min, while at 300°C it is barely complete after 3 hr. Using these data, pyrolyses at different temperatures were interrupted as soon as they were complete, and the resulting tars were analyzed for levoglucosan, its furanose isomer, and the yield of reducing sugars after hydrolysis. The results given in Table I show that with increasing oven temperature, the amount of tar is increased while the yields of levoglucosan, its furanose isomer, and the increase in reducing sugar after hydrolysis remain almost constant. The net effect is that increasing oven temperature results in a greatly enhanced rate of pyrolytic depolymerization without detrimental effect on product yields due to decomposition reactions.

It should be emphasized here that the value of total reducing sugar obtained after tar hydrolysis does not correspond directly to D-glucose content. It is known that the tar and its polymeric components contain carbonyl groups, derived from dehydration and rearrangement,<sup>39</sup> which analyze as reducing sugar. In these experiments the reducing power of the tars before hydrolysis was about  $9 \pm 2\%$  of the total reducing sugar determined after hydrolysis. Since only trace amounts of free glucose are found in tars from cellulose pyrolysis,<sup>10,12</sup> this reducing power can be attributed to other components, such as 3-deoxy-D-gly-

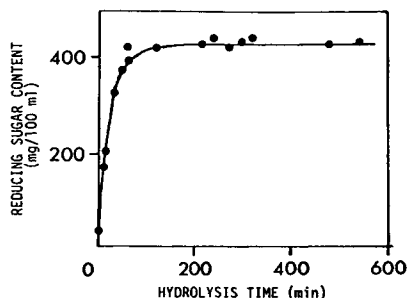


Fig. 1. Hydrolysis of tar from pyrolysis of cellulose (Whatman CF 11, Lot A) with 1N H<sub>2</sub>SO<sub>4</sub> at 97°C.

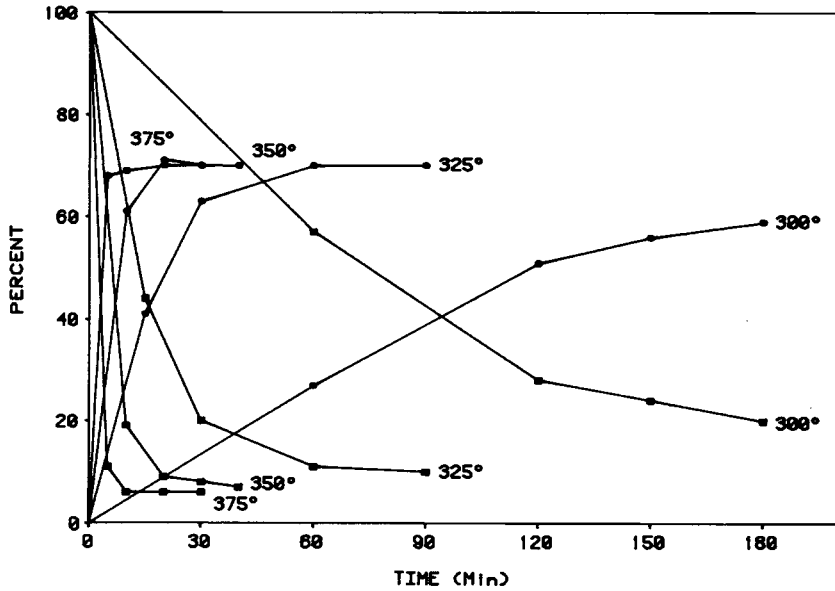


Fig. 2. Residue (■) and tar (●) from pyrolysis of cellulose powder under vacuum from 300–375°C.

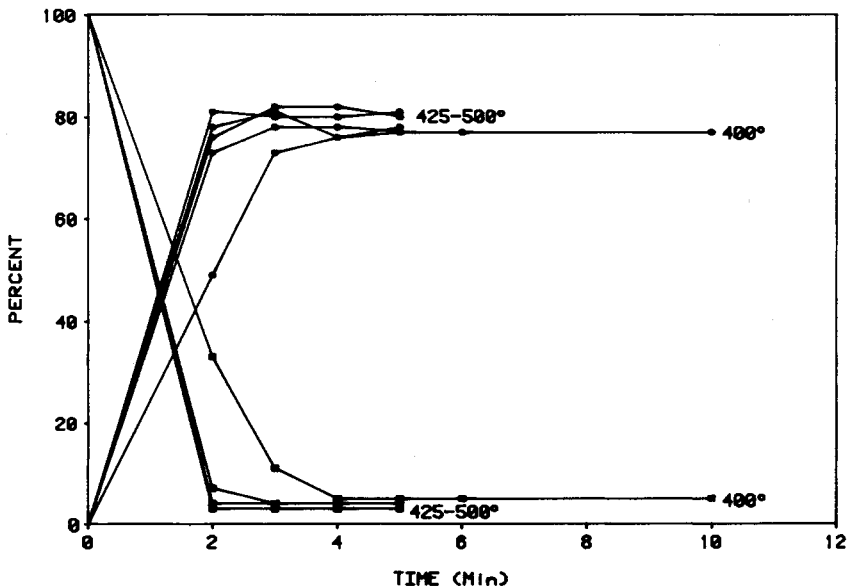


Fig. 3. Residue (■) and tar (●) from pyrolysis of cellulose powder under vacuum from 400–500°C.

cerohexosulose, 1,5-anhydro-4-deoxy-D-glycerohex-1-en-3-ulose, and other aldehydic substances which are known<sup>12,15</sup> to be present. The reducing sugar data given in Table I are corrected for this effect and represent the net increase in reducing power after hydrolysis of the tar. This increase, which was equivalent to a yield of  $58 \pm 2\%$  D-glucose for pyrolysis at or above 375°C, is in good agreement with the value obtained in a similar manner by Golova and co-workers<sup>4,16-18</sup> and reported as the levoglucosan yield. However, since some of the increased

TABLE I  
Effect of Temperature on the Products from Pyrolysis of Cellulose Powder<sup>a</sup> under Vacuum

Oven temperature °C	Pyrolysis time, min	Percent yield from cellulose				
		Char	Tar <sup>b</sup>	Levoglu- cosan	1,6-Anhydro- $\beta$ -D- glucofuranose	Reducing sugar <sup>c</sup>
300	180	21	60	34	4	47
325	60	10	70	38	—	54
350	30	8	70	38	4	52
375	10	6	70	38	—	59
400	5	5	77	39	4	60
425	4	4	78	40	4	59
450	3	4	78	39	4	57
475	3	3	80	38	4	58
500	3	3	81	38	4	57

<sup>a</sup> Whatman CF 11 powder, Lot A.

<sup>b</sup> Method A, see Experimental section.

<sup>c</sup> Increase in reducing sugar after tar hydrolysis.

TABLE II  
Effect of Temperature on the Products from Pyrolysis of Cellulose Powder<sup>a</sup> at Atmospheric Pressure under Nitrogen

Oven temperature, °C	Pyrolysis time, min	Percent yield from cellulose				Total reducing sugar <sup>c</sup>
		Char	Tar <sup>b</sup>	Levoglu- cosan	1,6-Anhydro- $\beta$ -D- gluco- furanose	
350	25	20	54	17	4	34
400	7	14	59	17	1	38
450	5	11	60	20	2	40
500	4	8	58	20	2	39

<sup>a</sup> Whatman CF 11, Lot A.

<sup>b</sup> Method A.

<sup>c</sup> After hydrolysis.

reducing power originates from the hydrolytic production of compounds other than glucose,<sup>39</sup> the actual glucose content of the hydrolyzed tars is less than the value indicated by the reducing sugar. This was confirmed by direct analysis of glucose in the hydrolyzate from tar produced at 400°C. This analysis showed an increased reducing power of 60% but an actual D-glucose content of only 49% (see Table III). These analytical subtleties should provide a key for better interpretation of the large volume of literature on this subject and help to solve some of the surrounding controversies.

In a complementary study using the same substrate,<sup>13</sup> a simple kinetic model was developed for pyrolysis of cellulose involving an initial activation stage followed by simultaneous depolymerization and decomposition reactions. Using the kinetic data obtained in that study, the linear relationship shown in Figure 4 between  $1/T$  and  $\ln t$  was obtained, where  $T$  is the pyrolysis temperature and  $t$  is the time required for 90%, 99%, and 99.9% completion of the pyrolysis. Due to the problems of heat transfer, this relationship is valid only up to about 340°C. Above that range the temperature of the substrate lags behind the oven temperature due to the endothermic evaporation of the pyrolysis products. This lag is accentuated at higher temperatures, when the sample may reach the oven

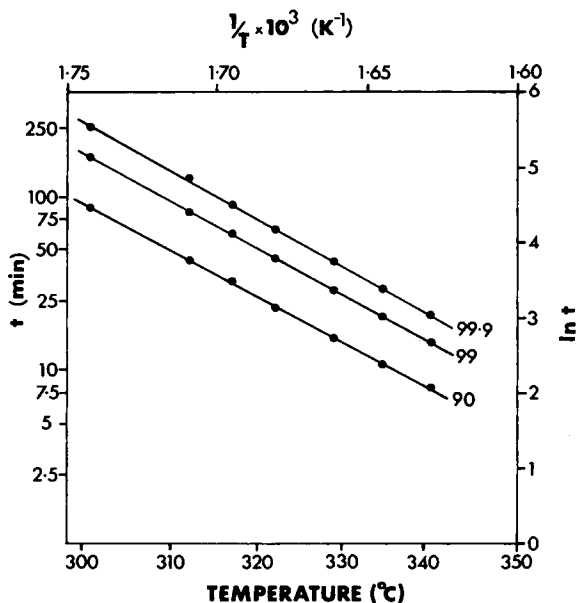


Fig. 4. Pyrolysis time required for 90%, 99%, and 99.9% degradation of cellulose powder (calculated from kinetic model).

temperature only when the pyrolysis is virtually complete. With the experimental conditions used in this study, the point of diminishing returns for raising the oven temperature was reached at about 425°C, when the reaction was complete in about 2 min, yielding 78% tar or 40% levoglucosan.

In the second phase of this investigation, the pyrolysis of cellulose powder was conducted in flowing nitrogen at atmospheric pressure. Weight loss and tar production were measured within the temperature range of 350–500°C. It was found that pyrolysis was complete in the same time period as the corresponding experiments under vacuum. However, as shown in Table II, more char and less tar (54–60%), levoglucosan (17%–20%), and reducing sugar were produced. These yields are substantially better than those previously reported<sup>10</sup> for pyrolysis of cellulose at atmospheric pressure because the tar was more effectively removed from the heated zone with a moving collection tube (see Experimental section). The levoglucosan yield was still only one half that obtained by pyrolysis under vacuum, in which the accelerated removal of volatile pyrolysis products from the heated zone reduces the opportunity for secondary decomposition.

### Pyrolysis of Different Types of Cellulose

Samples of a variety of readily available cellulose substrates were pyrolyzed under vacuum at 400°C. Pyrolysis times of 5–9 min were sufficient to ensure complete pyrolysis with minimal decomposition of the pyrolyzate. The results are summarized in Table III, in which the substrates are listed in order of decreasing yield of tar, levoglucosan, and 1,6-anhydro-β-D-glucofuranose and increasing yield of char.

The cellulosic samples gave yields of levoglucosan ranging from 14% to 58%. The yield of levoglucosan and its concentration in the tar increased with in-



TABLE III  
Products from Pyrolysis of Celluloses at 400°C under Vacuum

Substrate	Percent yield from cellulose					Levoglucosan concentration in tar, %
	Char	Tar <sup>a</sup>	Levoglucosan	1,6-Anhydro- $\beta$ -D-glucofuranose	D-Glucose after (hydrolysis)	
Cotton hydrocellulose	2	85	58	6	77	68
Baker microcrystalline	3	83	51	5	—	61
Avicel microcrystalline	3	84	49	5	—	58
Whatman CF 11, Lot A	5	69	39	4	49	57
Whatman No. 41 filter paper	5	69	38	4	—	55
Cotton linters	5	64	30	3	—	47
Whatman CF 11, Lot B	7	58	29	3	—	50
Cotton fabric	9	46	14	1	—	30

<sup>a</sup> Method B, see Experimental section.

creasing tar yield from each sample. Thus, the substrate had a strong influence on the course and products of pyrolysis. This substrate dependence is especially evident in the 29% and 39% yields of levoglucosan obtained from two different lots of Whatman CF 11 powder, a product of relatively high purity, having a maximum ash content of 0.015%. These data indicate one reason why such a wide range of levoglucosan yields has been reported in the literature.

The tars from cotton hydrocellulose and Whatman CF 11, Lot A, were hydrolyzed and the resulting glucose contents were determined. It is evident that for both substrates the amount of glucose formed exceeded the content of levoglucosan and its furanose isomer in the tar, showing that a portion of the glucose was derived from other hydrolyzable components of the tar.

The substrates which gave the best yields of levoglucosan on pyrolysis are produced by partial acid hydrolysis, whereas the cotton linters and fabric samples which gave low yields had not been treated with acid. Venn,<sup>27</sup> in his early semiquantitative studies, observed that inorganic impurities in raw cotton, seen as ~1% ash content, greatly impaired levoglucosan production. Improved yields were obtained if the cotton was first washed with distilled water, but best yields were obtained after dilute alkali and then dilute acid washing which reduced the ash content to ~0.04%. Golova and co-workers<sup>3</sup> similarly concluded that relatively minor inorganic contaminants catalyzed extensive degradation of the cellulose and greatly reduced the yield of substances in the tar that were hydrolyzable to reducing sugar.

It was thus of interest to determine if improved yields of levoglucosan could be obtained from the substrates that had given the lowest yields, i.e., cotton fabric and Whatman CF 11 (Lot B), after they had been washed with water or with dilute acid. The results in Table IV show that while a wash with boiling distilled water did result in increased yields of tar and levoglucosan, much more dramatic increases were brought about by a dilute acid wash followed by rinsing with distilled water to neutrality. In fact, acid-washed substrates gave yields of levoglucosan only slightly lower than those from the microcrystalline celluloses. Pyrolyzates from the acid-washed substrates also afforded more than 50% yield of glucose upon hydrolysis.

The question raised by these experiments is whether the improved yields of

TABLE IV  
Effect of Prior Washing with Water or Acid on the Pyrolysis of Cellulose at 400°C under Vacuum

Substrate	Pretreatment	Percent yield from cellulose				
		Char	Tar <sup>a</sup>	Levoglucosan	1,6-Anhydro- $\beta$ -D-glucofuranose	D-Glucose (after hydrolysis)
Whatman CF 11, Lot B	Untreated <sup>b</sup>	7	58	29	3	—
	Water wash <sup>c</sup>	4	70	33	3	—
	1% H <sub>2</sub> SO <sub>4</sub> wash <sup>d</sup>	5	79	48	7	68
Cotton fabric	Untreated <sup>b</sup>	10	46	14	1	—
	Water wash <sup>e</sup>	9	59	28	2	—
	1% H <sub>2</sub> SO <sub>4</sub> wash <sup>d</sup>	5	73	42	4	52
	5% H <sub>2</sub> SO <sub>4</sub> wash <sup>d</sup>	3	76	50	6	—

<sup>a</sup> Method B, see Experimental Section.

<sup>b</sup> As supplied, see Experimental Section.

<sup>c</sup> At 97°.

<sup>d</sup> At room temperature.

<sup>e</sup> Washed with boiling absolute ethanol, then water at 97°C.

levoglucosan are due to removal of inorganic impurities, addition of trace amounts of acid, or changes in the crystallinity or fine structure of the cellulose due to the acid-washing pretreatments. Whatever the cause, these results are of considerable practical significance.

### Thermal Analysis of Cellulose Substrates

Thirteen cellulose substrates were subjected to thermal analysis (DTA and DTG). All substrates produced DTA curves of similar shape; however, the data in Table V show that the relative endothermic peak areas were larger with substrates which yielded more levoglucosan. As shown in Figure 5, the enthalpy change represented by the peak area increases in a linear fashion with the increased yield of levoglucosan produced on vacuum pyrolysis. The cotton linters sample had an inconsistently low endothermic peak area. This voluminous substrate was the only one which was difficult to pack into the aluminum sample pan, suggesting that sample density and convection factors affect the efficiency of heat transfer. For this reason, data from the linters was not used in determining the best-fit line by least-squares analysis in Figure 5.

There is also a good linear correlation between the yield of levoglucosan and the temperatures of the DTA and DTG peaks, which represent the maximum rates of heat and weight loss. As shown in Figure 6, the lower peak temperatures correspond with increased levoglucosan production. This correlation is difficult to explain because when these peak temperatures are lowered in cellulose pyrolysis by the catalytic effect of inorganic additives (e.g., flame retardants), production of levoglucosan is drastically reduced and the decomposition reactions are enhanced.<sup>2</sup> This anomalous behavior might arise from the ability of inorganic compounds to catalyze transglycosylation as well as dehydration and other decomposition reactions.<sup>40</sup>

While an explanation for these results is not available at this time, the corre-

TABLE V  
Comparison of Thermal Analysis Data with Levoglucosan Production at 400°C

Substrate	Percent yield of levoglucosan	Rel. <sup>a</sup> DTA endotherm peak area	DTA endotherm maximum, °C	DTG weight-loss maximum, °C
Cotton hydrocellulose	58	2.32	340	349
Baker microcrystalline	51	2.17	347	
Cotton fabric, 5% H <sub>2</sub> SO <sub>4</sub> washed	50	1.81	348	
Avicel microcrystalline	49	1.82	349	352
Whatman CF 11, Lot B, 1% H <sub>2</sub> SO <sub>4</sub> washed	48	1.88	346	
Cotton fabric, 1% H <sub>2</sub> SO <sub>4</sub> washed	42	1.69	357	
Whatman CF 11, Lot A	39	1.88	355	
Whatman No. 41 filter paper	38	1.81	357	365
Cotton linters	30	0.83	365	368
Whatman CF 11, Lot B	29	1.67	370	375
Cotton fabric, water washed	28	1.25	369	
Cotton fabric	14	1.05	382	388
Whatman No. 1 filter paper <sup>b</sup>	8	1.00	380	

<sup>a</sup> Based on peak area for Whatman No. 1 filter paper = 1.00.

<sup>b</sup> Pyrolyzed at 500°C.

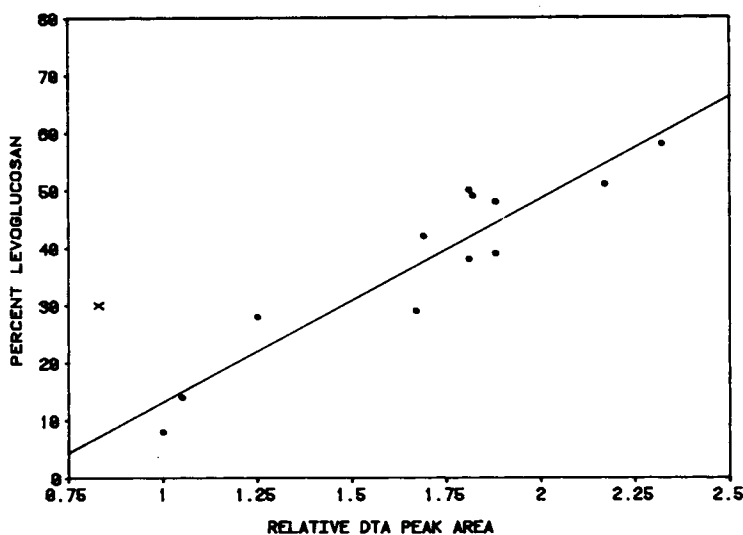


Fig. 5. Correlation between yield of levoglucosan on vacuum pyrolysis and relative DTA endothermic peak area for various cellulose substrates, where peak area for Whatman No. 1 filter paper is taken as 1.00. The best-fit line ( $r^2 = 0.87$ ), excluding data for cotton linters (x), is shown.

lation of thermal analysis data and levoglucosan production may prove useful in rapidly screening potential pyrolysis substrates.

### Wood-Derived Materials

Definition of optimal conditions for pyrolysis of pure celluloses, discussed above, provides basic information for the pyrolytic conversion of commonly available cellulosic materials, mainly wood and waste paper.

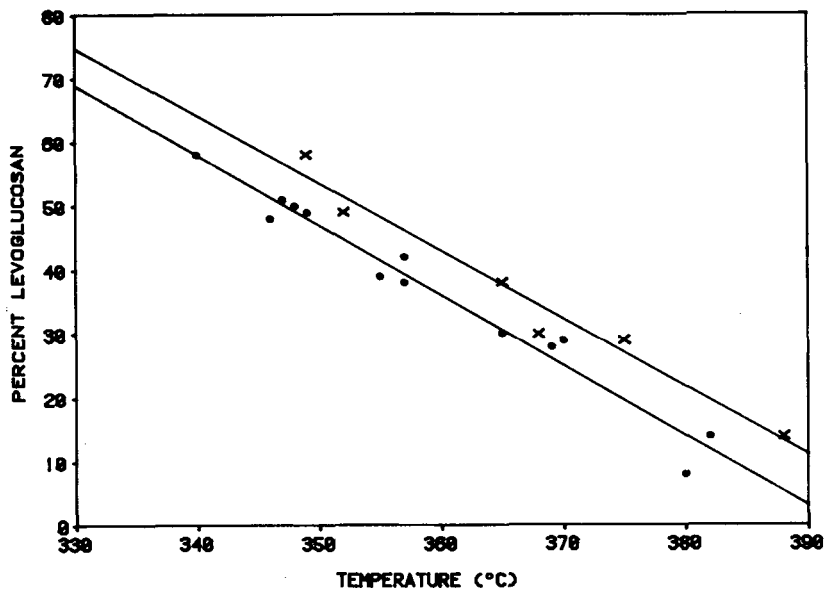


Fig. 6. Correlations between yield of levoglucosan on vacuum pyrolysis and the temperature of the endothermic maximum in the DTA curve (●) and the maximum rate of weight loss in the DTG curve (×). The best-fit lines ( $r^2 = 0.97$  in both cases) are shown.

Waste paper is a difficult substrate to define since its composition is dependent upon the pulping process and source of raw materials. Despite the expected inconsistencies, production of levoglucosan from newsprint and kraft paper was investigated because of the potential industrial importance of these substrates. As shown in Table VI, pyrolytic yields of levoglucosan (4%) and reducing sugar (13%–16%) from these substrates were very low.

Western cottonwood, *Populus trichocarpa*, was selected as a typical low-grade hardwood. The composition of this substrate has been determined in this laboratory<sup>41</sup> as 44% cellulose, 25% lignin, 21% O-acetyl-4-O-methylglucuronoxylan, and 10% glucomannan. The ground, extracted cottonwood contained inorganic impurities which would be expected to interfere with levoglucosan production. Although pyrolysis of this material gave considerable tar (47%), the yield of levoglucosan was quite low—only 3% from wood, or 6% from its cellulose portion.

TABLE VI  
Products from Pyrolysis of Cellulosic Materials<sup>a</sup> at 500°C

Substrate	Percent yield from substrate			
	Char	Tar <sup>b</sup>	Levoglucosan	Total reducing sugar <sup>c</sup>
	Pyrolysis under Vacuum			
Newsprint, Lot A	8	50	4	15
Kraft paper	11	39	4	13
	Pyrolysis at Atmospheric Pressure under Nitrogen			
Newsprint, Lot A	15	44	4	16
Kraft paper	15	36	4	13

<sup>a</sup> Ground to 40 mesh.

<sup>b</sup> Method A, see Experimental section.

<sup>c</sup> After hydrolysis.

Pretreatment of the wood by washing with dilute sulfuric acid resulted in consistently better yields of levoglucosan, but for a reason not yet understood, there was considerable variation between different batches, and yields of levoglucosan from the cellulose portion of the wood ranging from 20% to 40% were obtained. The data shown in Table VII for acid-washed cottonwood represent the case of minimum improvement.

The possibility that the lignin or hemicellulose components of the whole wood might be interfering with levoglucosan production was examined. Removal of most of the lignin by acid chlorite treatment provided a cottonwood holocellulose substrate (56% cellulose), while removal of most of the "xylan" component by prehydrolysis with dilute acid provided a cottonwood lignocellulose substrate (59% cellulose). The initially isolated holocellulose had a 0.87% ash content and gave little levoglucosan on pyrolysis, but pretreatment involving dilute alkali and then dilute acid washes reduced the ash content to <0.05% and increased the attainable yield of levoglucosan to 51% based on the cellulose content. The lignocellulose was immediately suitable for pyrolysis, having an ash content <0.05%, and provided a 57% yield of levoglucosan based on the cellulose content, or 25% yield from the original wood. D-Glucose yields of 71% and 78%, based on the cellulose components, were obtained after mild acid hydrolysis of the tars from the low ash holocellulose and lignocellulose substrates. The acid-washed cottonwood gave D-glucose yields of 30% to 70% from different batches. It appears, then, that the depolymerization of cellulose to levoglucosan can occur satisfactorily in the presence of lignin and hemicellulose and that the difficulties encountered in the pyrolysis of whole wood are due to other factors.

While the sugar yields (i.e., levoglucosan and D-glucose) reported for the acid-washed cottonwood are far superior to any previously reported for whole

TABLE VII  
Pyrolysis of Wood-Derived Materials at 400°C Under Vacuum

Substrate	Percent yield from substrate (or from cellulose portion, shown in parentheses)					
	Ash	Char	Tar <sup>a</sup>	Levoglucosan	1,6-Anhydro-β-D-glucofuranose	D-Glucose (after hydrolysis)
Cottonwood						
Untreated <sup>b</sup>	0.59	16	47	3(6)	trace	5(12)
1% H <sub>2</sub> SO <sub>4</sub> wash	<0.05	12	52	9(20)	0.6(1.5)	14(31)
Cottonwood lignocellulose						
Untreated <sup>c</sup>	<0.05	18	71	34(57)	3(6)	46(78)
Cottonwood holocellulose						
Untreated <sup>d</sup>	0.87	21	21	1(1)	trace	1(2)
1% NaOH, then 1% H <sub>2</sub> SO <sub>4</sub> washes	<0.05	9	65	29(51)	3(6)	40(71)
Newsprint						
Untreated, Lot B	—	12	39	2	0.3	—
1% H <sub>2</sub> SO <sub>4</sub> wash	—	19	43	15	2	—
1% HCl wash	—	14	56	19	2	—

<sup>a</sup> Method B, see Experimental section.

<sup>b</sup> Extracted and washed with water.

<sup>c</sup> Filtered from dilute sulfuric acid reaction mixture and washed with water to neutrality.

<sup>d</sup> Washed with water only.

wood, the sugar yields from lignocellulose are far more promising. In this case the prehydrolysis of hemicelluloses gives xylose, the cellulose component is converted efficiently to glucose derivatives, and the remaining char, which is largely derived from the lignin component, has a good fuel value.<sup>42</sup> Pyrolysis of lignocellulose on a larger scale (11 g) afforded a tar containing 28% levoglucosan, or 48% based on the cellulose portion of the substrate. Crystallization from acetone at  $-35^{\circ}\text{C}$  yielded 18% crude levoglucosan, or 30% based on cellulose.

While pyrolysis of untreated newsprint gave very little levoglucosan, as shown in Table VII, washing with dilute acids markedly improved the yield. After a 1% sulfuric acid wash, a 15% yield of levoglucosan based on total paper was obtained, while a 1% hydrochloric acid wash afforded a 19% levoglucosan yield.

### CONCLUSIONS

It has been shown unequivocally that levoglucosan yields greater than 50% can be obtained from pyrolysis of pure cellulose under controlled conditions involving prior treatment of the substrate with dilute acid. While the commonly available cellulosic materials such as wood and newsprint provide very poor yields of levoglucosan, the yield could be greatly improved with the same dilute acid pretreatment. Pyrolysis of these pretreated materials may become attractive as an industrial process for the production of levoglucosan and/or glucose. Methanol, acetic acid, and char are possible by-products of this process.

Prehydrolysis of hardwoods with dilute acid provides a substrate which produces even greater yields of levoglucosan and glucose. The cellulose portion of the lignocellulose produced in this manner is converted to levoglucosan in 57% yield or, after mild acid hydrolysis, to D-glucose in 78% yield. D-Xylose and its acid-degradation product, furfural, from the prehydrolyzed "xylan" component are the potential by-products of this approach.

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