

Yields and Composition of Sirups Resulting from the Flash Pyrolysis of Cellulosic Materials Using Radiant Energy

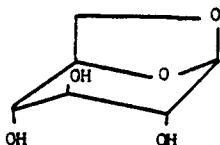
CHINE I. DE JENGA and MICHAEL JERRY ANTAL, JR.,* *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, N.J. 08544*, and MAITLAND JONES, JR., *Department of Chemistry, Princeton University, Princeton, N.J. 08544*

Synopsis

Cellulosic materials have been flash pyrolyzed using concentrated solar energy. The sirups obtained were composed mainly of levoglucosan. Radiant flash pyrolysis has thus been identified as a potentially attractive means of selectively degrading biomass material into good yields of relatively few products. The techniques and equipment employed to determine the composition of the pyrolyzates are described.

INTRODUCTION

The pyrolysis of cellulose and other biomass materials has been shown by Shafizadeh¹⁻⁹ and others¹⁰⁻¹⁵ to involve a complex series of competitive consecutive reactions. Thus, cellulose undergoes dehydration, elimination, breakage of C—O bonds along the chain and transglycosylation to yield hexose units that rearrange to form 1,6-anhydro- β -D-glucopyranose (1) (levoglucosan). Further degradation and condensation leads to the formation of carbon monoxide, carbon dioxide, water, methane, and numerous aldehydes, ketones, and acids.



(1)

Finally, intermolecular dehydration and crosslinking produce carbonaceous char.¹⁶⁻¹⁸ The number, type, and distribution of the different products depend on several variables. Temperature, heating rate, the environment (air, inert gas, or vacuum), residence time, and the absence or presence of inorganic salts, acids, bases, and other additives all play a prominent role.¹⁷⁻³⁰ It has also been shown that the structure, crystallinity, orientation, and crosslinking of cellulose have a considerable effect on the behavior of cellulosic materials upon pyrolysis.³¹⁻³⁴

* Present address: Department of Mechanical Engineering, University of Hawaii, Honolulu, HI 96822.

Various mechanisms have been put forward to account for the formation of the observed products. Broido et al.¹¹ have suggested that on heating, cellulose initially suffers chain cleavage to units of lower degree of polymerization (DP). These units subsequently decompose to levoglucosan. Still further heating causes the levoglucosan to decompose to the observed lower-molecular-weight products.^{14,27} Shafizadeh¹ has pointed out that levoglucosan is not necessarily the only primary product from which the secondary compounds are obtained. The decomposition of cellulose with evolution of lighter fractions starts before the formation of levoglucosan is observed. This observation has been explained by assuming the simultaneous depolymerization and decomposition of cellulose.

Research efforts in our laboratories³⁵⁻³⁷ have been directed toward the use of radiant (visible) light as a means of pyrolysis. The use of concentrated solar or visible radiation has been identified as an attractive and effective means of rapidly heating biomass and thereby achieving flash pyrolysis. Large quantities of condensible sirups with little or no char are produced. Conditions within the solar-fired chemical reactor can be manipulated to immediately condense these sirups intact, or to further pyrolyze the sirups and produce a hydrocarbon-rich synthesis gas. The sirups are a potentially rich source of fuels and chemicals, whereas the synthesis gas can be used directly as a fuel or to synthesize methane or methanol. Clearly, a knowledge of the mechanism of pyrolysis, based upon complete identification of the products of pyrolysis, is essential in understanding the parameters necessary to enhance the yields of the various products.

In the present study, biomass material was pyrolyzed using a solar-fired flash pyrolysis reactor. This report presents the analysis of the condensible sirups, and an attempt is made to explain the formation of the individual components on the basis of known reaction mechanisms.

EXPERIMENTAL

Pyrolysis of Biomass Material

The samples used in the pyrolysis included Avicel PH-102 powdered microcrystalline cellulose (FMC Corporation), hardwood lignum sawdust derived from maplewood and ground lignum corncob. The samples were fed into a quartz reactor located at the focal point of the solar furnace where the concentrated radiation achieved a flux density of ca. 125 W/cm². The volatile products produced by the rapidly pyrolyzing biomass were removed from the reactor by means of steam and collected in cooled collection vessels. The evolved gases were passed through Erlenmeyer flasks filled with glass beads and a demister filled with quartz wool prior to collection in Pyrex sample bulbs. The experimental procedure and apparatus have been previously described in detail.³⁵

After the experiment, the reactor and the collection vessels were washed first with water, then with a methanol/acetone mixture. The water wash and acetone/methanol wash were analyzed separately.

Conditions within the reactor were not well characterized because of the complexities of performing an experiment out of doors on the top of a 21-m tall tower. In addition, the vagaries of August weather in Atlanta permitted only a limited operating time, which was further abbreviated by financial constraints.

Detailed numerical simulations of the pyrolysis chemistry, heat, mass, and momentum transfer occurring within the reactor indicate that the biomass particles experienced a heating rate of about 8000°C/s to a stagnation temperature of about 600°C.³⁶ The residence time in the reactor was calculated to be about 0.2 s.³⁶ These values are strongly dependent upon the size, shape, absorptivity, and other physical characteristics of the individual particles fed into the reactor. Consequently, they should be considered to be order-of-magnitude estimates only.

The residence time was insufficient to effect complete pyrolysis of any of the materials studied; thus, the solids collected (see Table I) included both char and unpyrolyzed biomass. Spouted bed reactors are presently being developed and tested in this laboratory, which are not afflicted by these problems.³⁷

Analysis of Products

The analysis and identification of product gases (CO, CO₂, H₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈) and char from the pyrolysis of cellulose, sawdust, and corncob have been described.³⁵ The results are summarized in Table I. This report deals with the analysis of the condensible sirups obtained from the pyrolyzates.

The analyses were carried out by means of thin-layer chromatography (TLC), gas chromatography (GC), gas chromatography/mass spectrometry combination instrument (GC/MS), and infrared spectroscopy.

The general procedure consisted of treating the sirups with 2,4-dinitro-

TABLE I
Summary of Biomass Pyrolysis Test Results

Material	Cellulose	Corn cob	Hardwood
Gasification environment	Steam	Steam	Steam
Radiant flux level, W/cm ²	70	70	70
Solids feed rate, g/min	8.6	225.0	3.2
Steam flow rate, g/min	4.3	4.3	3.5
Inert purge rate, L/min	0.2	1.0	1.0
Exiting gas flow rate, L/min	4.0	2.3	3.5
Solids fed, g	ND	ND	89.6
Solids collected, g ^a	184	1085	41.8
Sirups collected, g	10.1	8.8	3.7
Gas production, L	5.2	2.2	30.45
Mass balance	ND	ND	0.94
Carbon balance	ND	ND	0.94
Gas calorific value, Btu/scf	495	387	488
Gas analysis, %: ^b			
CO	54.6	46.7	47.5
H ₂	20.3	13.4	21.8
CO ₂	5.8	26.1	10.9
CH ₄	12.1	8.5	13.0
C ₂ H ₄	5.7	4.7	4.3
C ₂ H ₆	0.6	0.1	0.4
C ₃ H ₈	0.3	0.3	1.3
C ₄	0.6	0.2	0.3

^a Solids collected included unpyrolyzed material.

^b By volume normalized to 100% by excluding N₂ purge gas and gases analyzed but not identified; ND = not determined.

phenylhydrazine in order to convert any carbonyl-containing products into their 2,4-dinitrophenylhydrazones. The resulting hydrazones were separated by TLC and identified by comparing their mobilities on TLC with those of known samples.^{26,28}

For GC analysis, the sirups were trimethylsilylated.^{39,40} An aliquot of the solution containing the sirups was evaporated to dryness under reduced pressure and treated with Sylon TP (pyridine + trimethylsilylimidazole, Supelco). To ensure complete silylation, the samples were treated with a large excess of the silylating reagent and allowed to stand at room temperature, with exclusion of moisture, for 30 min to overnight. The GC/MS analyses were performed on a Hewlett-Packard 5985A GC/MS system using a 6-ft ($\frac{1}{4}$ in. o.d., 2 mm i.d.) glass column packed with 3% OV-101 on 80–100 mesh Supelcoport. The carrier gas (helium) flow rate was adjusted to obtain optimum separation at 30 ml/min. The column temperature was programmed at 8°/min, 150–275°C. Alternatively, the unsilylated samples were separated on a 10-ft ($\frac{1}{8}$ in. o.d., 2 mm i.d.) stainless steel GC column packed with Chromosorb 101. The carrier gas and temperature were adjusted as above.

All the products were identified on the basis of their retention times and their mass-spectral fragmentation patterns. These were compared to the fragmentation patterns of authentic samples and with published spectral data.^{39,41–43}

PROCEDURES AND RESULTS

Cellulose Pyrolyzates

Water Wash Portion

An aliquot of the sirup solution in water was filtered and then treated with 2,4-dinitrophenylhydrazine. The resulting hydrazones were spotted on a TLC plate (silica) and developed with benzene–tetrahydrofuran (7:3) solvent system

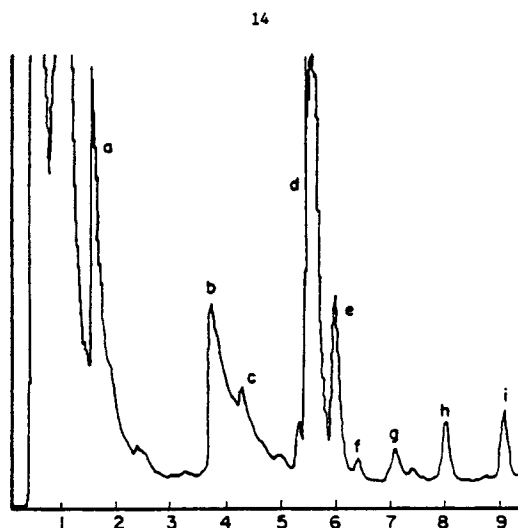


Fig. 1. GC-Chromatogram of Silylated Avicel sirup (water wash): a, 5-hydroxymethylfurfural; b, 3,6-anhydro- β -D-glucopyranose; c, 1,6-anhydro- β -D-glucofuranose; d, 1,6-anhydro- β -D-glucopyranose (levoglucosan); e, unknown; f, unknown; g, unknown; h, i, α - and β -D-glucose.

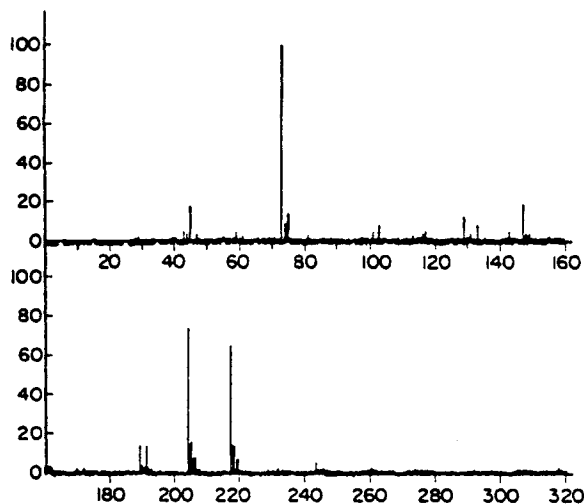


Fig. 2. Mass spectrum of silylated levoglucosan from cellulose pyrolyzate.

to give two major spots whose mobilities were identical to those of the hydrazones of levoglucosan and glucose. It would appear that under the reaction conditions, the sirup constituents undergo hydrolysis as does levoglucosan,^{26,38} to yield mainly glucose.

For GC/MS analysis, the solvent water was removed from the water wash under reduced pressure. The GC analysis of the distillate (Chromosorb 101) showed no evidence of the presence of solutes. The residue was treated with Sylon TP and chromatographed to give a well-resolved GC chromatogram (see Fig. 1) showing a preponderance of levoglucosan (1). The mass spectrum is shown in Figure 2. As expected, levoglucosan shows no molecular ion peak.^{39,41-44} The base peak occurs at m/e 73 and is due to the ion Me_3Si^+ . The two next most intense peaks (m/e 204 and 217) correspond to the ions $\text{Me}_3\text{SiO}-\text{CH}-\text{CHOSiMe}_3$ and $\text{Me}_3\text{SiOCH}=\text{CH}-\text{CHSiOMe}_3$, respectively.

The chromatogram peaks *h* and *i* were shown by their mass spectra to be due to α - and β -glucose. It has been shown^{39,40} that trimethylsilylation of glucose in the presence of pyridine causes anomerization. In our case, these anomers have not been assigned, but their mass spectra are identical [Figs. 3(a) and 3(b)]. Peaks *a*, *b*, and *c* (Fig. 1) were identified by comparison of their retention times with those of authentic samples.

Table 2 lists the products obtained from the trimethylsilylated sirups. The quantities quoted are based on percent by weight of the total sirup yield.

Acetone/Methanol Wash

The solvent was evaporated and the residue treated with 2,4-dinitrophenylhydrazine, as detailed above. The TL chromatogram matched that of the water wash portion.

The silylated residue gave a gas chromatogram (Fig. 4) with two fewer peaks than that of the water wash portion.

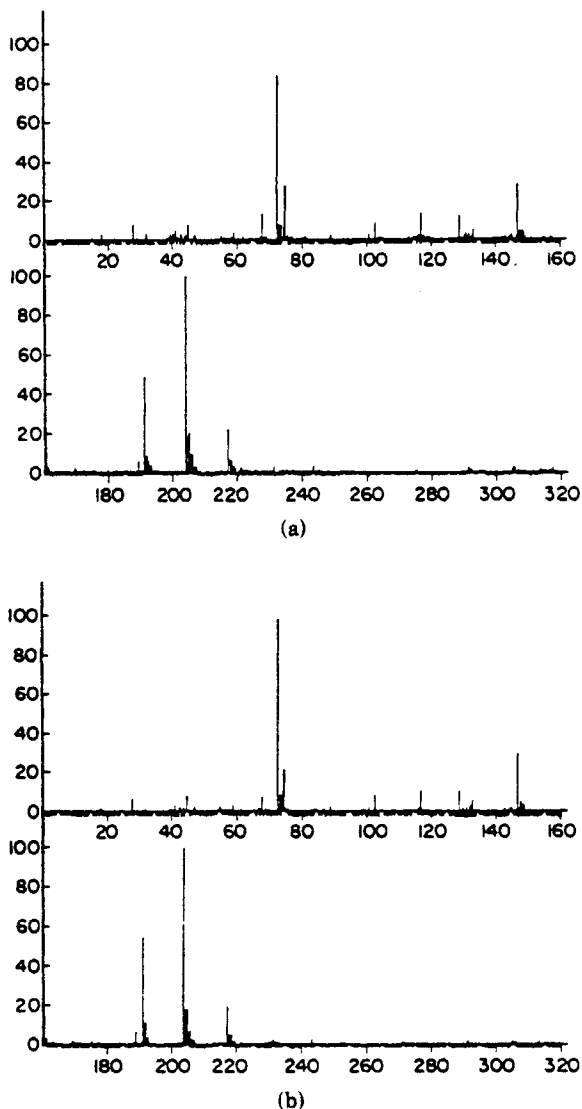


Fig. 3. Mass spectrum of trimethylsilylated glucose with GC Retention time of: (a) 8.1 min, (b) 9.1 min.

Hardwood Pyrolyzates

Water Wash Portion

Treatment of the solution with 2,4-dinitrophenylhydrazine and comparative TLC, as described earlier, indicated the presence of a reducing sugar hydrolyzable to glucose. This showed that the wood pyrolyzate contained levoglucosan and/or glucose.

Trimethylsilylation of the sirup obtained after removal of the solvent water and subsequent GC analysis gave a chromatogram (Fig. 5), with the major peak being the same as that obtained from cellulose. Two additional peaks (*b* and *c* in Fig. 5), however, occurred. The yields of the constituents (Table II) were much less than those obtained in the case of cellulose.

TABLE II
Summary of the Sugar-Related Products of Biomass Pyrolysis (Percent Yields)

Product	Cellulose		Hardwood H ₂ O wash
	H ₂ O wash	Me ₂ CO wash	
5-Hydroxymethylfurfural	15.3	—	5.6
3,6-Anhydro- β -D-glucopyranose	14.1	—	4.9
1,6-Anhydro- β -D-glucofuranose	0.4	6.6	0.17
1,6-Anhydro- β -D-glucopyranose	40.9	39.2	5.5
α - and β -D-Glucose	6.5	9.8	0.95

Acetone/Methanol Wash

The infrared spectrum of the crude sirup showed strong absorption bands due to hydroxyl and carbonyl groups as well as aromatic bands. The ¹H nuclear magnetic resonance (NMR) spectrum of the crude substance in deuterated acetone, though not very well resolved, showed resonance peaks in the aromatic region and very broad peaks higher upfield. This indicated the presence of substituted aromatic compounds. The gas chromatogram of the unsilylated sirup showed a minimum of 16 peaks, only four of which have been tentatively identified on the basis of their mass-spectral fragmentation patterns.⁴¹ These are vanillin (2) [*m/e* 152 (M⁺, 100%), 151, 137, 124, 109, 81], coniferyl alcohol (3) [*m/e* 180 (M⁺), 152, 150, 137, (100%), 124, 109, 91], 4-propylguaiaicol (4) [*m/e* 166 (M⁺), 137 (100%), 109, 94, 81], and coniferylaldehyde (5) [*m/e* 178 (M⁺, 100%), 152, 89, 76] (See Scheme I). These products derive from the degradation of the lignin in the wood, which is made up of high-molecular-weight phenolic compounds.⁴⁵

The sirup also contains a trace of levoglucosan as evidenced by the gas chromatogram of the silylated material.

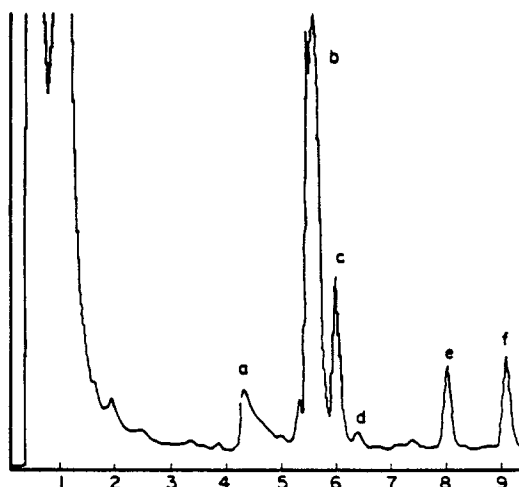
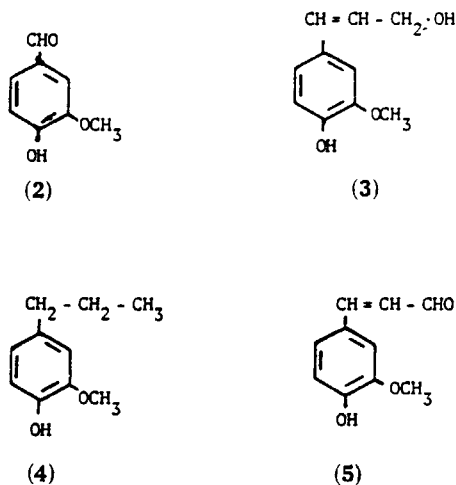


Fig. 4. Gas chromatogram of silylated Avicel pyrolyzate (acetone-methanol wash): a, 1,6-anhydro- β -D-glucofuranose; b, 1,6-anhydro- β -D-glucopyranose (levoglucosan); c, unknown; d, unknown; e, f, α - and β -D-glucose.



Scheme I.

DISCUSSION

The analysis of the sirups (summarized in Table II) clearly indicates that, of the identified constituents, levoglucosan (1) is the dominant product. Unfortunately, absolute yields of the sirups could not be calculated because the biomass underwent only partial pyrolysis and the amount of solids fed for two of the experiments was not determined because of a malfunctioning screw feeder.³⁵ More recent research using a spouted bed reactor has overcome these weaknesses.³⁷

The general reactions occurring when cellulosic materials are pyrolyzed have been characterized as "primary" and "secondary."¹ Primary reactions lead to the formation of the first volatile products, which undergo further pyrolysis into secondary products.¹⁻²⁰ Results summarized in Tables I and II indicate that a fraction of the primary volatile products passed through the reactor intact,

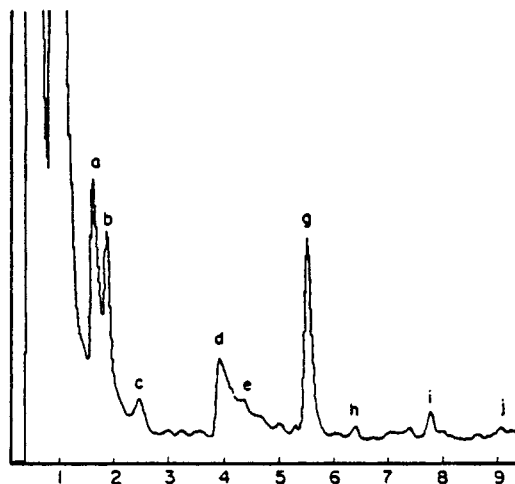


Fig. 5. Gas chromatogram of silylated sirup obtained from the pyrolysis of hardwood lignum sawdust: *a*, 5-hydroxymethylfurfural; *b*, unknown (xylose?); *c*, unknown; *d*, 3,6-anhydro- β -D-glucopyranose; *e*, 1,6-anhydroglucofuranose; *f*, 1,6-anhydroglucopyranose (levoglucosan); *h*, unknown; *i*, *j*, α - and β -D-glucose.

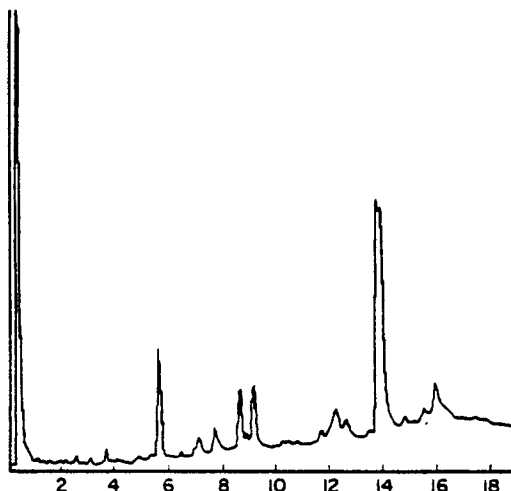


Fig. 6. Gas chromatogram of hardwood lignum sawdust pyrolyzate: acetone-methanol wash.

whereas the remainder suffered further pyrolysis resulting in the observed yields of permanent gases. The evident role of secondary reactions in the final product distribution has been ascribed to one unfortunate aspect of the reactor design. Because the entering cold biomass particles flowed countercurrent to the upward-moving hot pyrolytic vapors, some of the vapors doubtlessly condensed on the particles and were recycled into the reactor. Consequently, the yield of sirups was considerably reduced. Nevertheless, the specificity of the reactor, evidenced in Table II by the high concentration of relatively few sirup constituents, gives cause for optimism regarding the ultimate potential of solar-fired flash pyrolysis reactors to produce high yields of monomeric sirups from biomass materials.

CONCLUSIONS

Concentrated solar energy can be used to effect the rapid pyrolysis of biomass particles in a continuously fed chemical reactor. Chemical analyses described in this report suggest that the pyrolysis process results in the selective formation of levoglucosan from cellulose and of similar monomeric fragments from wood. In the present reactor embodiment, these primary pyrolysis products were subject to recycling and further pyrolysis due to the countercurrent flow of gases and solids in the reactor. Future reactors utilizing cocurrent flow conditions are expected to produce large yields of relatively few monomeric fragments which reflect the chemical composition of the biomass feedstock. These sirups seem likely to become a rich feedstock for the production of fuels and chemicals from renewable resources.

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