Carbohydrate Research, 158 (1986) 253–261
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Rapid hydrothermolysis of cellulose and related carbohydrates

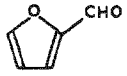
R. KRISHNA M. R. KALLURY, CHRIS AMBIDGE, THOMAS T. TIDWELL,
Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1 (Canada)

DAVID G. B. BOOCOCK, FOSTER A. AGBLEVOR, AND DANIEL J. STEWART
Department of Chemical Engineering and Applied Science, University of Toronto, Toronto, Ontario M5S 1A4 (Canada)

(Received December 20th, 1985; accepted for publication in revised form, June 25th, 1986)

The degradation of cellulose has been receiving considerable attention both as an alternative energy source and for the production of useful chemicals, including sugars[1–4]. Methods that have been utilized include direct pyrolysis[4–9], hydrothermolysis[10], and enzymic degradation[11]. Hydrothermolysis involves heating the substrate with water, with or without an added catalyst, and summaries of several investigations of hydrothermolysis of cellulose have appeared[12–15]. In experiments using a flow system, so that the soluble products were quickly removed from the heated reactor, D-glucose was the major initial product, with a maximum yield[12] of 42.6% at 264°. Other carbohydrates and 5-(hydroxymethyl)-2-furaldehyde (**1**) were also significant products[12] below 275°. The major products reported from cellulose and pure water after 2.5 min at 300° were **1** (30%), 2-furaldehyde (**2**, 13%), and 30% of carbohydrates[15].

1

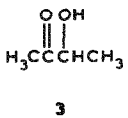


2

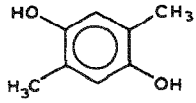
Hydrothermolysis of cellulose in the presence of base[13–18] led to a different range of products, including simple aliphatic ketones and phenols. The formation of 2,5-dimethylhydroquinone (**4**) from acetoin (**3**) was demonstrated, and a reasonable pathway for the conversion of D-glucose into **3** and then of **3** into **4** was proposed[15].

The hydrothermolysis of cellobiose below 250° was examined[19] under conditions similar to those used for cellulose[12], and the former reaction also yielded mainly D-glucose, along with **1** and other products, with D-glucose reacting further

0008-6215/86/$ 03.50



3



4

under the same conditions, to give **1**, **2**, and a variety of compounds having lower molecular weights.

We have undertaken a systematic study of the hydrothermolysis of cellulose and related sugars over the temperature range of 250 to 350°, in order to ascertain the thermolysis products and elucidate their mechanism of formation. A recently developed, fast-heat-up, tubular reactor system[20] was utilized for these studies, in order to minimize residence-time and effects due to reactions during heat-up and cool-down.

RESULTS AND DISCUSSION

The weight % of the various product fractions (see experimental section for the fractionation procedure) from the hydrothermolyses of D-glucose, maltose, methyl α- and β-D-glucopyranosides, cellobiose, and cellulose are shown in Fig. 1(A–D). The major individual components of the chloroform-soluble oil-phase and the ether-soluble aqueous phase are presented in Table I, and structures are indicated in **5–8**. The products from the basic hydrothermolyses are included in

TABLE I

COMPOSITION[a] OF ETHER AND $CHCl_3$ EXTRACTS FROM NEUTRAL HYDROTHERMOLYSIS

Products from ether extracts	*295°*[b]						*350°*					
	G	*M*	*α*	*β*	CL	CB	G	M	*α*	*β*	CL	CB
1	6.4	6.0	6.9	6.0	10.8	6.6	0.2	3.0	0.5	1.2	2.1	0.5
2	4.8	3.0	4.6	2.0	5.4	4.5	1.1	3.0	3.9	2.5	4.2	4.0
5	0.2	0.03		0.3	0.4	0.8	1.1	1.0	1.3	2.0	2.1	1.9
6	0.5	0.05	1.4	1.0	2.1	1.4	0.7	1.0	1.0	0.1	1.0	0.5
Other	1.9	0.1	2.0	0.9	3.1	0.7	1.9	1.2	2.1	2.2	4.5	3.1
Products from $CHCl_3$ extracts												
1	3.1	5.0	1.0	5.1	5.0	8.4	0.8	3.0	3.1	1.8	1.9	0.5
2	2.7	2.0	1.0	2.0	1.2	2.8	2.4	3.0	3.6	2.0	2.9	1.9
7		0.01					0.4	0.5			2.0	0.1
5		0.02	0.1		0.2	0.3	4.8	3.0	2.3	1.3	2.0	4.7
8		0.01					0.4	0.3				0.1
Other	0.6	1.0	1.6	1.0	1.6	1.9	9.8	5.0	7.3	2.4	4.3	5.0

[a]Key: G, D-glucose; M, maltose; α, methyl α-D-glucopyranoside; β, methyl β-D-glucopyranoside; CL, cellulose; and CB, cellobiose. [b]About 10% more of **1** is observed for G, M, and α with D_2O as reactant.

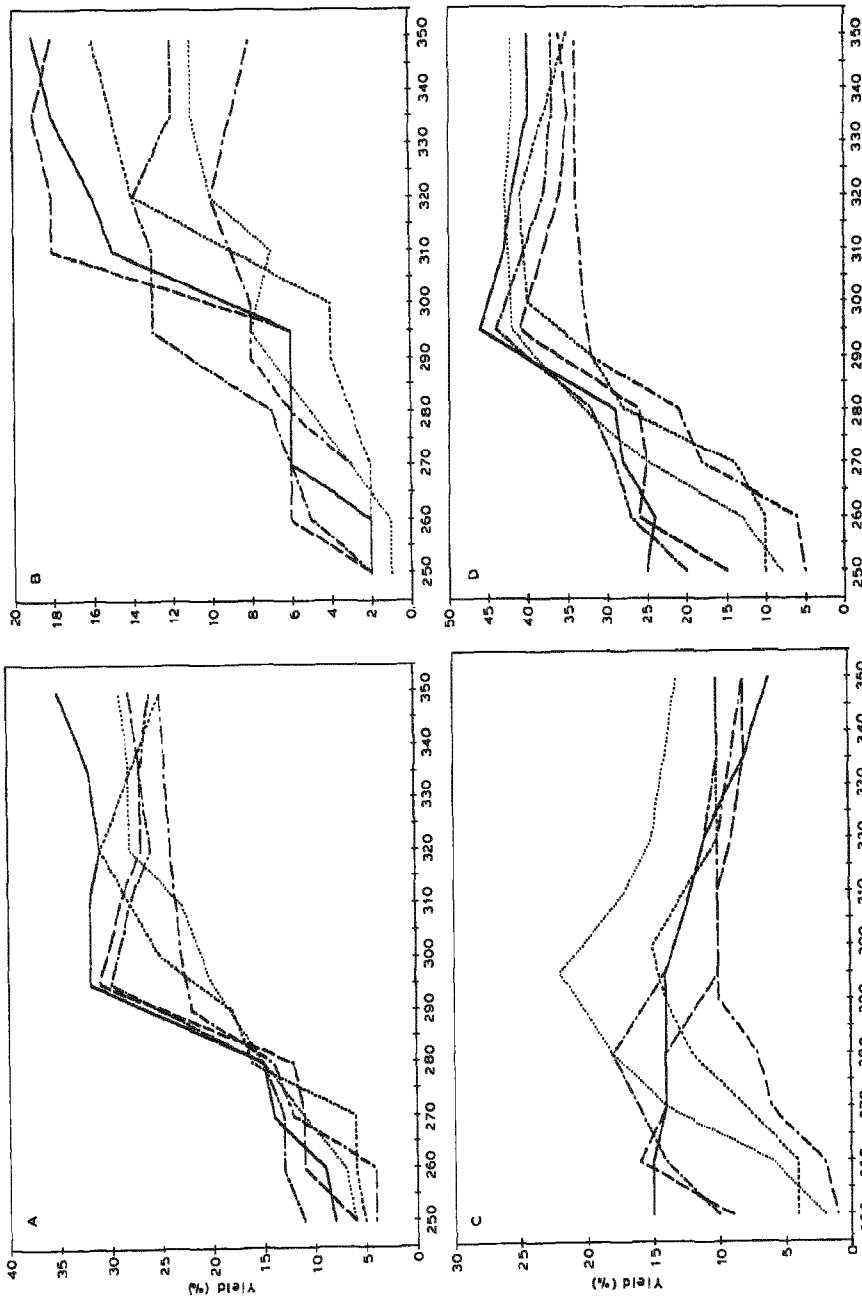
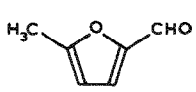
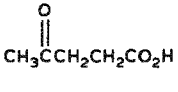


Fig. 1. Yield (%) of products *versus* temperature (°C). [A, total acetone-soluble oil; B, chloroform-soluble oil; C, aqueous-phase, ether-soluble compounds; D, total yield of oil. Key: ——, Glc; —·—, maltose; ----, methyl α-D-glucopyranoside; ——, methyl β-D-glucopyranoside; ...., cellulose; and ——, cellobiose.]

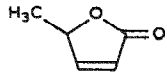


5



6

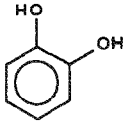
7a



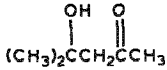
7b

8

9



10



11

TABLE II

COMPOSITION OF ETHER AND $CHCl_3$ EXTRACTS FROM BASIC HYDROTHERMOLYSIS[a]

Products from ether extracts	*295°*				*350°*			
	G	M	CL	CB	G	M	CL	CB
Acetic acid	3.2	4.0	1.7	1.6	3.0	4.0	1.2	1.3
C_3–C_5 acids	2.1	2.0	1.2	0.8	2.9	3.0	1.2	1.1
Catechol (**10**)	2.1	3.0	1.0	0.7	4.0	5.0	2.0	1.5
Hydroquinone (**9**)	0.3	0.1	0.3	0.5	0.1	0.1	0.3	0.2
Biacetyl (**8**)	1.9	1.0	0.5	1.1	0.3	0.1	0.2	0.2
Acetoin (**3**)	1.0	3.0	0.8	1.2	0.4	0.2	0.2	0.3
Other	5.3		0.5	2.0	4.1		0.9	2.3
11[b]	3.1		0.8		1.2			1.0
Products from $CHCl_3$ extracts								
11[b]	4.0	5.0	3.0	4.5	6.4	6.0	3.6	4.0
Catechol (**10**)	1.7	2.0	1.0	1.0	0.2	2.0	1.3	2.0
Me-catechols	3.4	3.0	1.8	2.0	5.6	5.0	2.6	3.5
Hydroquinone (**9**)	0.4	0.5	0.3	0.5	0.6	0.5	0.7	1.4
Me-hydroquinones	1.0	2.0	0.6	0.8	1.8	2.0	1.7	1.7
Other	3.8	3.2	2.2	0.6	2.7	0.5	2.2	1.4

[a]Negligible amounts of soluble products were obtained from methyl α- and β-D-glucosides. [b]Diacetone alcohol (**11**) was also identified in the product, as it has been by previous workers[33,34], but it has not been rigorously established whether this material is derived from the reactant or from the acetone used in the extraction.

TABLE III

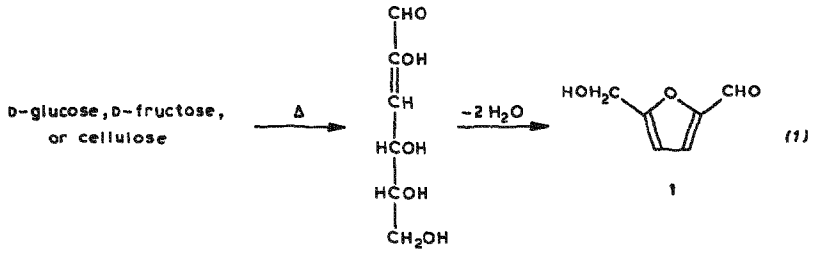
HYDROTHERMOLYSIS OF 5-(HYDROXYMETHYL)-2-FURALDEHYDE (**1**)

Temp. (°C)	**1** *recovered (%)*	**2**	**5**	**6**	**7**[a]	CH_3CO_2H
295	80	<1	5	10	5	—
350	60	<1	12	8	7	3

[a]Isomers not differentiated.

Table II (formulas **9–11**). The reaction of **1** under the hydrothermolysis conditions at 295 and 350° was also examined, and the product compositions observed are given in Table III.

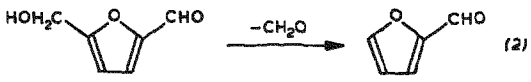
In agreement with previous workers[12–15], we confirmed that, under neutral conditions, 5-(hydroxymethyl)-2-furaldehyde (**1**) and 2-furaldehyde are significant products, as well as lesser proportions of 5-methyl-2-furaldehyde (**5**) (see Table I). Important evidence for the mechanism of formation of these products was the finding of Katō and Komorita[21] that 3-deoxy-D-*erythro*-hexosulose (**12**) is formed on pyrolysis of D-glucose, D-fructose, or cellulose at 220 and 260°, and these authors proposed the mechanism in Eq. *1*, involving **12**, to account for the formation of **1**.



12 1 (1)

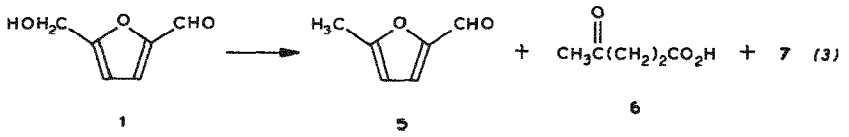
Previously, Katō had reported[22] that pyrolysis of **1** gives 2-furaldehyde (**2**) and 5-methyl-2-furaldehyde (**5**) in the ratios of 1:9.9 and 1:5.0 at 350 and 500°, respectively. On the basis of this observation, it was suggested[21] that **1** is not a major precursor of **2** on pyrolysis of hexoses, but rather, that the hexose is first degraded to a pentose, which then forms a deoxypentose analogues to **12** and that this cyclizes to **2**. The nature of the hexose-to-pentose conversion was not specified[21].

Later, the thermolyses of levoglucosan[23] (**13**) and of D-glucose[24,25] labeled with ^{14}C at various positions were studied; it was found that the loss of C-6 from these precursors, giving formaldehyde, is the major route for the formation of **2**, and, on this basis, it was proposed that **1** is the precursor to 2-furaldehyde (see Eq. *2*). A similar mechanism was then accepted by Ohnishi *et al.*[26]. Thus, there is a conflict between the earlier indication[21,22] that **1** is not the major precursor to **2**, and the more recent proposals that the route of Eq. *2* is followed[23–26].



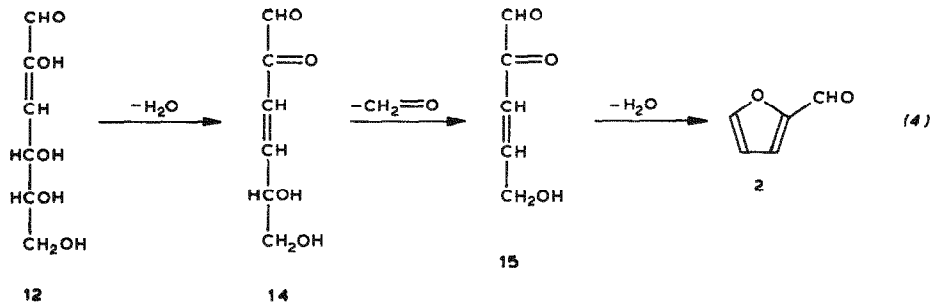
1 2 (2)

Our results (see Table III) show that **2** is not a significant product from the hydrothermolysis of **1**, and that 5-methyl-2-furaldehyde (**5**), and levulinic acid (**6**), and its lactone (**7**) are, instead, the major products (see Eq. *3*). The predominant formation of **5** relative to **2** agrees with the results of a previous study of this reaction[22], and the conversion of **5** into **6** and **7** is well documented[27,28].



1 5 6

The origin of this discrepancy between both of our observations which support the earlier reports[21,22] and the other interpretations[23–26] is of some interest. It is possible that different pathways are followed under the previous conditions and under ours. It appears more likely that, even though the results of the ^{14}C-labeling studies were consistent with the intermediacy of **1**, another path was actually followed. Such an alternative path would be the dehydration of **12** to **14**, which then loses formaldehyde in a reverse-aldol reaction to give **15**, which cyclizes to **2** with loss of a final molecule of water. The reverse-aldol cleavage is a familiar process in carbohydrate chemistry[15,29], and the cyclization of **15** to **2** is closely analogous to the conversion[30] of D-xylose into **2**. The route of Eq. *4* appears to accommodate all of the published data on the conversion of **13** and D-glucose into **2**, in particular, the findings, based on ^{14}C-labeling, that loss of C-6 is the major route to **2**. In view of the failure of **1** to give major amounts of **2**, it seems that Eq. *4* should be considered the major route to **2** from thermal treatment of the hexoses, as well as of cellobiose and cellulose. The major difference between this scheme and the previous conclusion[23–26] is the timing of the loss of formaldehyde relative to cyclization.

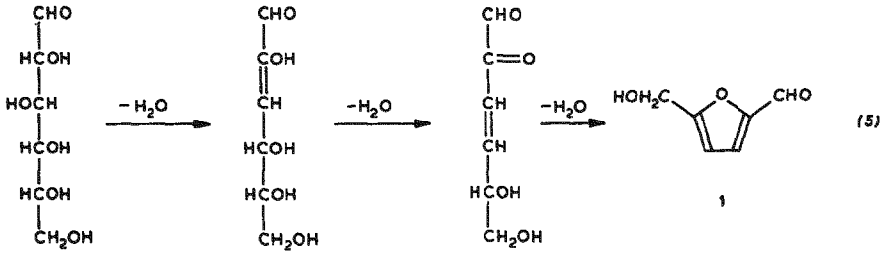


12 14 15 2 (4)

The interesting question remains as to how the conversion of **1** into **5** occurs under these conditions. Possibly, acetoin (**3**), which has been identified as a product during cellulose liquefaction, serves as the reducing agent in this transformation. The reducing activity of acetoin in the formation of 2,5-dimethylhydroquinone (**4**) has been reported[31].

We also observed that a change in the reaction medium from H_2O to D_2O at 295° increases the yield of $CHCl_3$-soluble oil from D-glucose, maltose, and possibly, methyl α-D-glucopyranoside as well, but does not affect the other sugars, or the reactions in sodium carbonate (see Fig. 1, A–D). The additional material appears as **1** (see Table I), but this product had not added any deuterium according to the

mass-spectral analysis. The origin of this increased yield is of some interest, and may involve a combination of solvent isotope-effects on the formation of **1**. The mechanism of this process, starting with D-glucose in acid, is accepted[31] to be that shown in Eq. *5*.



This sequence involves numerous proton-transfer steps, each with its own isotope effect, and consequently, the net solvent isotope-effect of the overall process is hard to predict. Reactions of the glycosides will involve additional steps in cleaving the glycosidic bonds, and further isotope effects are likely to appear here as well. Thus, although the observed effect of the isotopic nature of the solvent on the product composition is difficult to interpret on the molecular level, this effect may be of some diagnostic value in study of carbohydrate liquefaction, and, with further investigation, may become interpretable in terms of specific chemical processes.

In summary, the rapid hydrothermolysis of carbohydrates gives products whose composition is strongly dependent upon the particular precursor, as well as other reaction variables. The identity of the reaction products and the pathways to these materials have been clarified. This method shows great promise for elucidating the course of carbohydrate pyrolysis and for its practical application.

EXPERIMENTAL

Maltose, D-glucose, cellobiose, methyl α-D-glucopyranoside and 5-(hydroxymethyl)-2-furaldehyde (**1**) were obtained from Aldrich. Cellulose was BDH Avicel microcrystalline material, and methyl β-D-glucopyranoside was obtained from Sigma.

The rapid heat-up system[20] consisted of a stainless-steel, tubular reactor (15 cm long, 12 mm i.d.; 10-mL capacity), with air-tight, stainless-steel screw-fittings at each end. A thermocouple attachment measured the temperature inside the reactor.

The desired carbohydrate (1 g) and distilled water (5 mL) were placed in the reactor, which was flushed three times with nitrogen and sealed off. The reactor was then lowered into a pre-heated sand-bath (at 250 to 350°, as desired), and as soon as the contents attained the required temperature (1.5–2.5 min), it was taken out of the sand bath and plunged into cold water. The gases were vented, and the

aqueous layer decanted. The heavy, oily material adhering to the bottom of the reactor was mixed with acetone (20–25 mL), and the suspension filtered under gravity, to remove char and other suspended matter. The filtrate was evaporated, and the residue weighed, to give the total yield of oil. The residue was then extracted with $CHCl_3$ (4 × 25 mL) and the extract filtered under gravity. The weight of the $CHCl_3$-soluble oil was obtained after evaporation of the solvent. It was then subjected to preliminary gas–liquid chromatographic examination and the F.t.i.r. and ^1H- and ^{13}C-n.m.r. spectra were recorded. Finally, the $CHCl_3$-solubles were screened by g.l.c.–m.s. Where appropriate, the $CHCl_3$-soluble fraction was subjected to preparative gas–liquid chromatography, and the resulting fractions were examined by ^1H-n.m.r. spectroscopy and e.i.-m.s.

The aqueous phase was decanted at the conclusion of each reaction and was extracted with ether (4 × 25 mL); the extracts were combined, dried, evaporated, and the residue was analyzed as described for the $CHCl_3$ extract.

The products from five separate runs on each sugar were combined prior to analysis. The details of the instrumental analyses were described previously[32].

The residue from the extraction of the total, acetone-soluble oil by means of $CHCl_3$ was a dark-brown solid that contained no significant proportion of volatile material, and whose e.i.m.s. indicated the presence of polymeric material containing repeated furan units.

Each of the sugars was treated similarly in 5% Na_2CO_3, at 295° and at 350°, with 2-min heat-up times, and analyzed as before, except for the aqueous layers. These had a pH of 7.5 and were extracted with ether, acidified, and re-extracted with ether, so that two separate ether extracts were obtained, and these were analyzed separately.

ACKNOWLEDGMENTS

Financial support was provided by a Strategic Grant from the Natural Sciences and Engineering Research Council of Canada; by the Department of Energy, Mines, and Resources (Canada); by the Imperial Oil Company; and by a Canadian Commonwealth Scholarship to F.A.A.

REFERENCES

1 D. L. WISE (Ed.), *Bioconversion Systems*, CRC Press, Boca Raton, Florida, 1984.
2 D. L. KLASS, *Chemtech*, (1984) 486–491.
3 R. P. OVEREND, T. A. MILNE, AND L. K. MUDGE (Eds.), *Fundamentals of Thermochemical Biomass Conversion*, Elsevier, London, 1984.
4 F. SHAFIZADEH, *Pure Appl. Chem.*, 55 (1983) 705–720.
5 F. SHAFIZADEH AND T. T. STEVENSON, *J. Appl. Polym. Sci.*, 27 (1982) 4577–4585.
6 H. R. APPELL, Y. C. FU, S. FRIEDMAN, P. YAVORSKY, AND I. WENDER, *U. S. N. T. I. S., PB Rep.*, (1971) No. 203,669.
7 F. SHAFIZADEH, *Adv. Carbohydr. Chem.*, 23 (1968) 419–474.
8 R. H. FURNEAUX, J. M. MASON, AND I. J. MILLER, *J. Chem. Soc., Perkin Trans. 1*, (1984) 1923–1928.

9 G. N. RICHARDS, F. SHAFIZADEH, AND T. T. STEVENSON, *Carbohydr. Res.*, 117 (1983) 322–327.
10 C. J. BIERMANN, T. P. SCHULZ, AND G. D. MCGINNIS, *J. Wood Chem. Technol.*, 4 (1984) 111–118.
11 K. ERIKSSON, *Experientia*, 38 (1982) 156–159.
12 O. BOBLETER, R. NIESNER, AND M. RÖHR, *J. Appl. Polym. Sci.*, 20 (1976) 2083–2093.
13 P. M. MOLTON AND T. F. DEMMITT, *Polym.-Plast. Technol. Eng.*, 11 (1978) 127–157.
14 J. M. DONOVAN, P. M. MOLTON, AND T. E. DEMMITT, *Fuel*, 60 (1981) 898–902.
15 D. A. NELSON, P. M. MOLTON, J. A. RUSSELL, AND R. T. HALLON, *Ind. Eng. Chem. Prod. Res. Dev.*, 23 (1984) 471–475.
16 R. L. EAGER, J. M. PEPPER, J. C. ROY, AND J. F. MATHEWS, *Can. J. Chem.*, 61 (1983) 2010–2015.
17 J. A. RUSSELL, R. K. MILLER, AND P. M. MOLTON, *Biomass*, 3 (1983) 43–57.
18 P. M. MOLTON, R. K. MILLER, J. A. RUSSELL, AND J. DONOVAN, in D. L. KLASS (Ed.), *Biomass as a Nonfossil Fuel Source*, American Chemical Society, Washington, D.C., 1981; *ACS Symp. Ser.*, 144 (1981) 137–153.
19 O. BOBLETER AND G. BONN, *Carbohydr. Res.*, 124 (1983) 185–193.
20 D. BECKMAN AND D. G. B. BOOCOCK, *Can. J. Chem. Eng.*, 61 (1983) 80–86.
21 K. KATŌ AND H. KOMORITA, *Agric. Biol. Chem.*, 32 (1968) 21–26.
22 K. KATŌ, *Agric. Biol. Chem.*, 31 (1967) 657–663.
23 F. SHAFIZADEH AND Y. Z. LAI, *J. Org. Chem.*, 37 (1972) 278–284.
24 Y. HOUMINER AND S. PATAI, *Israel J. Chem.*, 7 (1969) 513–524.
25 Y. HOUMINER, in G. G. BIRCH AND L. F. GREEN (Eds.), *Molecular Structure and Function of Food Carbohydrates*, Wiley, New York, 1973, Chap. 9.
26 A. OHNISHI, K. KATŌ, AND E. TAKAGI, *Polym. J.*, 7 (1975) 431–437.
27 J. HORVAT, B. KLAIĆ, B. METELK, AND V. ŠUNJIĆ, *Tetrahedron Lett.*, (1985) 2111–2114.
28 P. E. SHAW, J. H. TATUM, AND R. E. BERRY, *Carbohydr. Res.*, 5 (1967) 266–273.
29 E. SJÖSTRÖM, *Wood Chemistry*, Academic Press, New York, 1981, pp. 134, 161.
30 M. S. FEATHER, D. W. HARRIS, AND S. B. NICHOLS, *J. Org. Chem.*, 37 (1970) 1606–1608.
31 D. A. NELSON, S. D. LANDSMAN, AND P. M. MOLTON, *Carbohydr. Res.*, 128 (1984) 356–360.
32 R. K. M. R. KALLURY, T. T. TIDWELL, AND D. G. B. BOOCOCK, *Anal. Chem.*, 55 (1983) 1689–1694.
33 R. K. MILLER, P. M. MOLTON, AND J. A. RUSSELL, in D. L. KLASS AND G. H. EMERT (Eds.), *Fuels from Biomass and Wastes*, Ann Arbor Science, 1981, Chapter 25, p. 455.
34 R. L. EAGER, J. F. MATHEWS, J. M. PEPPER, AND H. ZOHDI, *Can. J. Chem.*, 59 (1981) 2191–2198.