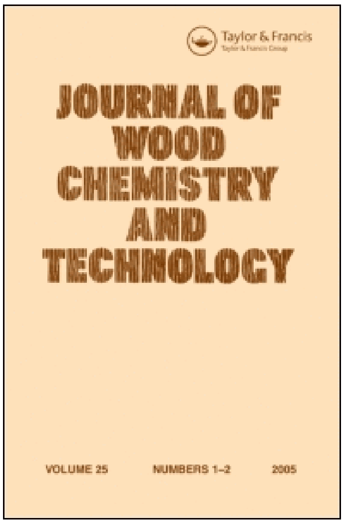

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Acid Catalyzed Degradation of Cellulose in Alcohols

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ACID CATALYZED DEGRADATION OF CELLULOSE IN ALCOHOLS

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ABSTRACT

Cellulose is degraded by alcohols and strong acid-catalysts at 180°C to 200°C within minutes. Alkylglucosides, 5-alkoxymethylfurfurals, and alkyl levulinates plus alkyl formates are formed in consecutive reactions, accompanied by some humic residue. The scope of the reaction was explored by using C_1-, C_2-, C_3-, and C_4-alcanols and by combining various lignocellulosic substrates with methanol. Effects of catalysts and co-solvents were tested, resulting in more selective reactions and suppressing dialkylether formation of the solvent. Yields of 46 % methyl levulinate, 44 % ethyl levulinate, and 37 % n-propyl levulinate (based on theory) from cellulose point to the preparative value of the reactions.

INTRODUCTION

At the turn of the century British researchers described for the first time the preparation of 5-bromo- and 5-chloro-methyl-2-furaldehyde from certain carbohydrates, including cellulose, by interaction with the hydrohalogenic acid in an inert solvent[1]. The products, formed by a hydrolysis-dehydration sequence, are very reactive and were obtained in modest yields. Later other workers improved the process by modifying the reaction conditions[2,3,4,5,6]. The facile conversion of 5-halomethylfurfurals into hydroxy-, acetoxy-, or alkoxymethylfurfurals by solvolysis reactions was also noticed very early[1,7,8,9]. 5-Alkoxymethyl-2-furaldehydes have also been reported as alcoholysis products from tetramethylfructose[10], fructose[11,12,13,14], glucose[11,14], saccharose[11,14], starch[11,14], and inulin[11,14]. The acid-catalyzed reactions can yield mixtures of alkoxymethylfurfurals and alkyl levulinates[11,13,14,15] or only alkyl levulinates[16] as a result of the decomposition of the furfural derivative to esters of levulinic and formic acid. Lower alkoxymethylfurfurals and alkyl levulinates, obtained from mono-, di- and polysaccharides, were also patented as tobacco flavorants[17].

Cellulose or cellulosic waste materials have apparently never systematically been subjected to acid-catalyzed degradation reactions in alcohols under severe conditions to prepare alkyl derivatives of hydroxymethylfurfural and levulinic acid[18]. Accordingly we started experiments of the alcoholysis of cellulose and certain lignocellulosic materials under conditions thought to optimize the formation of alkyl levulinates plus alkyl formates and/or alkoxymethylfurfurals. Patent protection for the process was applied for[19].

EXPERIMENTAL

Macherey-Nagel cellulose powder 300 HR, dried at 105°C, was used as the cellulose. Other substrates were technical samples. Alcohols, other solvents, and acids were reagent grade. 16.2 g of the cellulose substrate, 150 ml of an alcohol, and the specified amount of acid were placed in a teflon-lined autoclave with magnetic stirring (by Berghof Labortechnik, Eningen). After flushing with nitrogen und pressurizing to 0.8 MPa the autoclave was brought to the desired temperature by external heating, which took 28 ± 7 minutes. When the specified time had passed, the autoclave was cooled. Within 14 min temperatures below 150°C were reached. At room temperature the pressure was relieved through a gas washing bottle containing icecold water. The contents of the autoclave were then filtered. Washing with the alcohol and water left a black residue (humic acid) and some unreacted cellulose (1 to 3 %, except certain entries of Table 2). The filtrate was neutralized with sodium bicarbonate, treated with charcoal, and again filtered. From this solution the alcohol and low boiling products were removed by distillation. The residue (usually containing water) was extracted with ethyl acetate or dichloromethane 3 to 5 times. The combined organic layers, after drying with magnesium sulfate and evaporating the solvent, left an extract, which was characterized by ir and H-NMR spectra. Unequivocal assignments of NMR peaks, determining their integrals, and correcting for the hydrogen content of the compounds allowed quantification of the alkoxymethylfurfurals, alkyl levulinates, and furfural (as a minor product from a side-reaction) present. The analytical results were supported by the ir and uv spectra. From some selected extracts destillations in vacuo gave pure alkyl levulinates.

The extracted, aqueous phase, containing hydrophilic carbohydrates, after another purification with charcoal, was analyzed by the Orcinol-sulfuric acid method.

In the condensate containing the low boiling compounds, gc indicated the presence of the alkyl formate from the alcohol used and of the dialkylether, expected from dehydration of the solvent. This gc separation was achieved with a 9 ft column of Porapak Q at 180°C. Dimethylether was identified (by gc and H-NMR) and determined (gravimetrically) in the water of the washing bottle.

RESULTS AND DISCUSSION

To explore the scope of the reaction cellulose was subjected to degradation in various alcohols containing the same amount of sulfuric acid as catalyst. Table 1 contains repre-

TABLE 1

DEGRADATION OF CELLULOSE IN VARIOUS ALCANOLS CONTAINING 2 % H_2SO_4 1)

ENTRY	ROH	TIME (MIN)	TEMP. (°C)	HUMIC RESIDUE (A)	CARBO-HYDRATE IN H_2O (B)	FURFURAL (C)	ALKOXY-METHYL-FURFURAL (D)	ALKYL LEVU-LINATE (E)
1	CH_3OH	12	183	4.2	18.5	1.2	2.7	37.8
2	C_2H_5OH	9	195	15.4	4.0	0.5	1.6	38.4
3	N-C_3H_7OH	15	190	31.3	0.6	2.7	2.7	32.2
4	I-C_3H_7OH	15	196	33.7	0.2	2.0	1.2	22.3
5	N-C_4H_9OH	10	210	20.4	0.6	N.D.	N.D.	40.4
6	I-C_4H_9OH	15	211	20.0	0.2	N.D.	TR.	39.2
7	SEC. C_4H_9OH	15	188	39.2	0.2	2.0	4.6	27.4

1) 16.2 G CELLULOSE IN 150 ML SOLVENT

(A) % CARBON CONVERSION

(B) TO (E) % THEORETICAL MOLAR YIELD

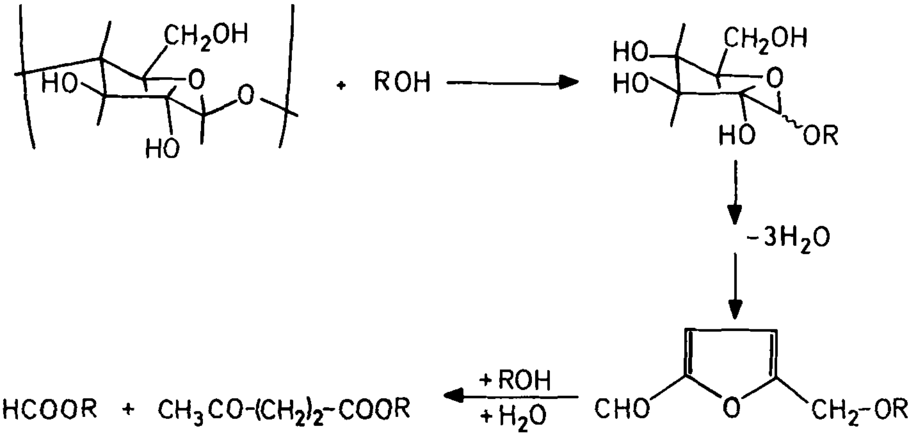

FIG.I

ACID-CATALYSED ALCOHOLYSIS OF CELLULOSE

sentative, but not optimized results. Higher alcanols require somewhat higher temperatures for a rapid and smooth reaction. As known from the degradations of cellulose in water, black solid residues (humic acid,a) are formed as by-products. The carbohydrate left in the aqueous phase (b) is largely a mixture of alkyl glucosides. Attempts to make it the main product are under way. The desired alkoxymethylfurfurals and alkyl levulinates are formed in various amounts, which can certainly be increased by optimal reaction conditions. The yields of the concurrently produced alkyl formates were not determined. An overall picture of the reaction sequence is depicted in Fig. 1.

An undesirable feature of the system is the acid-catalyzed side-reaction of the alcoholic solvent to yield the dialkyl-ether and, in the case of secondary alcohols, some alkene by dehydration. Milder reaction conditions are expected to diminish the ether formation from the alcanol.

Table 2 contains experimental results of cellulose degradations revealing the influence of the acidic catalysts on the product distribution. Dimethylether formation from methanol is suppressed by lowering the concentration of sulfuric acid (entries 1 to 4). However, most cellulose ends up in the aqueous phase under the milder conditions (compare entry 11). Other strong acids (like in entry 5) or weaker acids under forcing conditions (entries 6 and 12) result in similar product distributions as obtained from the reaction catalyzed by sulfuric acid, while hydrohalogenic acids cause only a partial solution of cellulose (entries 7, 8, 9). The enrichment of methoxymethylfurfural, less stable than methyl levulinate, has not yet been achieved in a satisfactory way.

Results of solvolysis-dehydration-reactions of cellulose in various mixtures of methanol and water are presented in Table 3. An obvious effect of a higher water content or a longer reaction time (entries 2 and 3) is more humic acid formation, i.e. a less selective reaction. Methoxymethylfurfural and hydroxymethylfurfural are derived from competing methanolysis and hydrolysis reactions. Their yields, related to the initial concentration of MeOH and H_2O, indicate that the reaction rate constant of the alcoholysis is 1.5 to 3 times higher than the corresponding rate constant for the hydrolysis, assuming the same order of reactions. A moderate content of water in methanol has accordingly little effect upon the yield of methoxymethylfurfural, and, as indicated by the figures of column f, on the yield of methyl levulinate. The effect of small amounts of water present in the alcohols of Table 1 (approx. 1 %) was thought to be negligible. The levulinic acid obtained in the purely aqueous system (last entry) is in line with literature reports (e.g.[20]).

More water in the solvent suppresses the equilibrium reaction of methanol to dimethylether:

$$2CH_3OH \rightleftharpoons CH_3\text{-}O\text{-}CH_3 + H_2O$$

TABLE 2

Methanolysis of Cellulose Catalyzed by Different Acids in Various Concentrations[1]

Entry	Acid	W/V %	Time (min)	Temp. (°C)	Dimethyl-ether[2]	Dis-solved cell. (%)	Humic residue (A)	Carbo-hydrate in H_2O (B)	Furfural (C)	MMF[3] (D)	Methyl levu-linate (E)
1	H_2SO_4	2.0	12	183	17.6	97	4.2	18.5	1.2	2.7	37.8
2	H_2SO_4	1.0	11	187	12.8	99	5.1	42.7	tr.	1.8	27.5
3	H_2SO_4	0.5	10	184	2.4	91	3.9	71.2	tr.	0.6	9.8
4	H_2SO_4	0.2	9	186	0.5	60	tr.	86.5	-	0.7	7.7
5	CF_3SO_3H	0.5	10	193	7.3	99	6.2	33.8	0.7	1.5	22.3
6	p-Tolyl-SO_3H	2.0	30	210	n.d.	99	17.2	2.0	n.d.	0.5	34.8
7	HBr	1.0	12	190	tr.	26	n.d.	n.d.	n.d.	n.d.	n.d.
8	HCl	1.0	12	193	tr.	19	n.d.	n.d.	n.d.	n.d.	n.d.
9	HCl	1.0	45	195	tr.	42	n.d.	n.d.	n.d.	n.d.	n.d.
10	SO_2	4.7	17	189	tr.	49	n.d.	n.d.	n.d.	n.d.	n.d.
11	SO_2	5.9	66	191	0.2	83	tr.	89.1	0.1	0.3	7.3
12	SO_2	4.3	75	210	n.d.	98	24.9	12.3	tr.	0.6	18.2

1) 16.2 g cellulose in 150 ml methanol

2) wt% of methanol

3) Methoxymethylfurfural

(A) % Carbon conversion

(B) to (E) % theoretical molar yield

TABLE 3

Solvolysis of Cellulose in Methanol-Water Mixtures Containing 2 % $H_2SO_4$1)

Entry	Vol% 2) MeOH	Vol% 2) H_2O	Time (min)	Temp. (°C)	Dimethyl-ether3)	Humic residue (A)	Carbo-hydrate in H_2O (B)	Furfural (C)	MMF4) (D)	HMF5) (E)	Methyl levu-linate (F)
1	100	0	12	183	17.6	4.2	18.5	1.2	2.7	0	37.8
2	95	5	7	187	n.d.	4.7	58.0	tr.	1.9	tr.	33.3
3	95	5	23	187	18.8	11.3	6.5	tr.	1.2	tr.	47.2
4	90	10	8	188	8.5	5.8	48.1	0.6	1.6	0.4	30.2
5	80	20	8	190	4.0	7.4	64.5	tr.	1.7	0.8	23.9
6	70	30	8	189	n.d.	11.1	66.1	tr.	1.1	1.1	18.1
7	50	50	10	193	0.4	10.3	37.1	tr.	1.3	1.0	22.66)
8	25	75	13	184	n.d.	18.1	32.0	tr.	0.2	0.4	10.37)
9	0	100	10	197	0	25.9	5.7	0	0	0.6	45.08)

1) 16.2 g cellulose in 150 ml solvent

2) Water from the dehydration of methanol increases the H_2O concentration during the reaction

3) wt% of methanol

4) Methoxymethylfurfural

5) Hydroxymethylfurfural

6) Plus 11.3 % levulinic acid

7) Plus levulinic acid, n.d.

8) Levulinic acid

(A) % Carbon conversion

(B) to (F) % theoretical molar yield

As a bimolecular reaction, dilution of methanol (or another alcanol) by any other solvent is expected to reduce the unwanted dialkylether formation more than the alcoholysis of cellulose, which is first order in ROH.

To test this assumption and the effect of less polar co-solvents the reactions in Table 4 were performed. The decreased yields of dimethylether prove that the dehydration can effectively be reduced. Moreover, all additions of very low polar co-solvents to methanol or ethanol (Table 5) caused faster degradations of carbohydrates, reflected in low yields of water-soluble products (b), in accordance with earlier observations[18]. Increased yields of levulinic acid esters are the consequence. Unfortunately also the formation of undesired humic residues (a) is promoted in less polar media. The entries 10, 11, and 12 of Table 4 reflect results from a system with two liquid phases, one aqueous, the other organic. It is conceivable that a less stable intermediate, formed in the aqueous phase, is instantly extracted into the organic phase and thus accumulated. The yields of products (c) and (d) are indeed somewhat increased but not dramatically. The instability of the furfurals make their enrichment difficult. It is questionable if reactions of cellulose in alcohols involving strong acids and relatively high temperatures are suitable to optimize the formation of furfurals. Also the results of Table 5 involving ethanol - and especially entries 5 and 6 - make it clear that the composition of the solvent exerts a great influence upon the product ratio of furfural to levulinic acid derivative.

Having established the conditions of a smooth and fast degradation of cellulose in alcohols, the reactions were extended to other substrates, rich in cellulose and available as forest or agricultural raw or waste material. Table 6 contains initial results of methanolysis of some lignocellulosic substrates. The expected molecules from the degradation of the hexosanes are formed, with methyl levulinate as the

TABLE 4

METHANOLYSIS OF CELLULOSE IN MIXED SOLVENTS1)

ENTRY	MEOH VOL%	CO-SOLVENT VOL%		TIME (MIN)	TEMP. (°C)	DIMETHYL-ETHER2)	HUMIC RESIDUE (A)	CARBO-HYDRATE IN H_2O (B)	MMF3) (C)	HMF4) (D)	METHYL LEVU-LINATE (E)
					WITH 2 % H_2SO_4						
1	100	0		12	183	17.6	4.2	18.5	2.7	0	37.8
2	50	50	CYCLOHEXANE	3	208	N.D.	24.5	1.3	0.4	0	37.1
3	50	50	TOLUENE	7	195	N.D.	16.9	3.2	1.8	0	39.8
4	50	50	CCl_4	5	194	N.D.	19.8	1.2	TR.	0	45.5
5	35	65	CCl_4	6	197	3.3	25.0	0.8	0.3	0	35.3
6	20	80	CCl_4	6	196	1.2	29.8	0.3	0.8	0	42.3
					WITH 0.5 % H_2SO_4						
7	100	0		10	184	2.4	3.9	71.2	0.6	0	9.8
8	50	50	CCl_4	12	182	0.9	2.7	59.0	2.2	0	13.3
9	20	80	CCl_4	6	188	0.4	22.4	2.6	4.9	0	46.6
10	32	65 3	CCl_4 H_2O	9	196	0.7	13.0	3.5	8.5	1.5	43.0
11	47	47 6	CCl_4 H_2O	8	199	0.5	5.7	29.4	6.0	1.5	36.8
12	45	45 10	CCl_4 H_2O	13	188	0.6	2.0	36.6	7.4	2.0	21.3

1) 16.2 G CELLULOSE IN 150 ML SOLVENT

2) WT% OF METHANOL

3) METHOXYMETHYLFURFURAL

4) HYDROXYMETHYLFURFURAL

(A) % CARBON CONVERSION

(B) TO (E): % THEORETICAL MOLAR YIELD

TABLE 5

Ethanolysis of Cellulose in Mixed Solvents Containing 0.5 % H_2SO_4 1)

Entry	EtOH Vol%	Co-solvent Vol%		Time (min)	Temp. (°C)	Humic residue (a)	Carbo-hydrate in H_2O (b)	Furfural (c)	EMF 2) (d)	Ethyl levulinate (e)
1	100	0		10	195	8.7	45.9	1.3	6.5	20.3
2	50	50	Cyclohexane	7	198	15.6	6.5	2.3	11.8	35.7
3	50	50	Toluene	8	212	19.6	0.7	tr.	6.9	41.1
4	50	50	CCl_4	7	202	9.4	1.5	tr.	10.0	43.3
5	50	50	$(C_2H_5)_2O$	12	185	11.4	56.7	tr.	11.1	15.2
6	50	50	p-Dioxane	8	195	5.6	30.2	2.6	10.9	8.7
7	50	50	Methylisobutylketone	9	200	1.1	18.5	-	7.3	32.2

1) 16.2 g cellulose in 150 ml solvent

2) Ethoxymethylfurfural

(a) % Carbon conversion

(b) to (e) % theoretical molar yield

TABLE 6

Methanolysis of Various Lignocellulosics and Carbohydrates1)

Entry	Substrate	Concentration of: Substrate	H_2SO_4	Time (min)	Temp. (°C)	Humic residue (a)	Carbo-hydrate in H_2O (b)	MMF2) (c)	Methyl levulinate (d)
1	Sulfite pulp from beech	5.4	4.0	6	186	4.8	9.7	tr.	30.6
2	Beech meal	5.5	2.0	15	175	7.6	39.7	0.7	10.1
3	Bagasse	5.3	2.0	8	193	5.1	8.4	0.8	19.1
4	Wheat straw	5.3	2.0	4	203	15.5	7.9	0.7	17.9
5	Barley straw	5.4	2.0	8	195	9.6	14.0	0.9	16.3
6	Fluff from waste paper	5.3	1.0	2	202	17.3	16.1	1.2	18.5
7	Wheat meal	10.7	2.0	15	187	1.7	13.7	1.6	31.4
8	Methyl-α-D-glucopyranoside	16.6	2.0	4	193	2.3	15.4	0.7	39.0

1) in 150 ml methanol. All yields in wt% of dry substrate.

2) Methoxymethylfurfural

main product. Furfural concurrently formed from the pentosanes was not determined. An industrial process of converting lignocellulosics to "oxychemicals" by alcoholysis would, of course, aim at using all components of the raw material, possibly in stages of increased severity. The "methanolysis" of wheat meal (entry 7) confirms early reports of degrading starch in alcohols[11,14]. It is interesting that the degradation of the monomeric glucoside (last entry) does not result in a better yield of levulinate than the methanolysis of the polymeric cellulose.

Of the many interesting applications of levulinic acid and its esters[21,22] one of the more tempting is the conversion to α-angelicalactone, which has been described as a fuel extender[23] and also as a versatile chemical intermediate.

The experimental work is continued to improve the conversions to the alkylglucosides or to the alkoxymethylfurfurals under milder experimental conditions. Also kinetic and mechanistic investigations are intended.

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