The Behavior and Derivatizations of Carbohydrates in Hydrogen Fluoride

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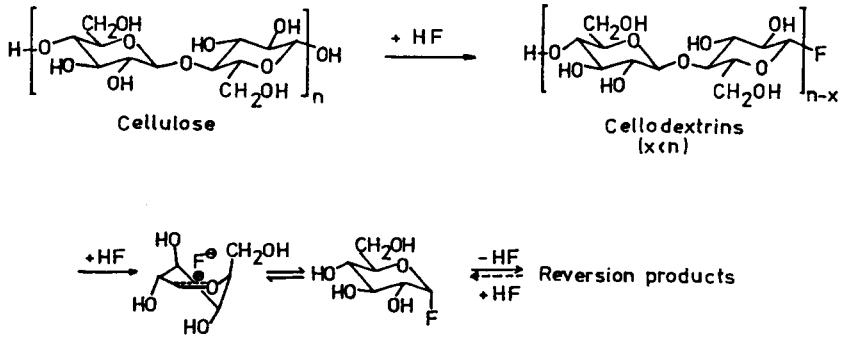
Synopsis

Low molecular weight β, 1 → 4-glucans (cellodextrins) are favorably prepared by cleavage of cellulose in liquid hydrogen fluoride at temperatures between −15 and −30 °C. This is due to the suppression of the reversion reaction in that low temperature range. Under conditions favorable for reversion the presence of water leads to a competing hydrolysis and lowers the average degree of polycondensation. For the preparation of defined *O*-glycosides from glucose and alcohols, hydrogen fluoride is not suitable as a reaction medium. Under reversion conditions, monohydroxy compounds are inferior in their reactivity to the competing carbohydrate molecules, and polyols like sorbitol furnish mixtures of isomeric glycosides. Gaseous hydrogen fluoride represents a highly suitable agent for the degradation of carbohydrate and lignin containing biomass, such as waste wood, for the purpose of providing fermentation raw material. As a model, lignocellulose was studied and the heat of reaction of the hydrogen fluoride sorption and desorption processes were examined. The practically important desorption value was found to be approximately 870 kJ/kg HF.

INTRODUCTION

Fifty years ago, glucose, starch and cellulose were reacted with liquid hydrogen fluoride for the first time by Helferich, Fredenhagen, and their co-workers.[1] Their conclusions, as well as the findings of later investigators,[3-5] were confirmed only recently by Pedersen's ^{13}C-NMR analysis in the reaction medium.[2] It was found that glycoside bonds undergo a hydrofluorolytic cleavage but can be rebuilt in a concentration-dependent equilibrium. In the case of a high HF/carbohydrate weight ratio, glucosyl fluoride is present almost exclusively; at a low ratio a mixture of oligomeric saccharides (reversion products) will predominate. By evaporation of hydrogen fluoride the equilibrium is further shifted towards the reversion products' side.



Scheme 1

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The equilibrium mixture can be analyzed also after precipitation of the carbohydrates by the addition of diethyl ether[1-4] or after a rapid neutralization of the mixture by means of solid calcium carbonate.[5]

The ^{13}C-NMR spectra predominantly afford information about the linkage patterns at the anomeric sites of glucose or the anhydroglucose monomer units, respectively. Additional evidence can be achieved by the use of the methylation analysis which allows us to investigate the glycosidic structure of the reversion products in more detail. It can be shown that the $1 \rightarrow 6$ glycosidic bond is prevailing by far and that branching occurs to a considerable amount. According to expectation, on only short contact with hydrogen fluoride or at low temperatures can partial retention of the structural features of the starting material be observed (cf. example amylose/cellulose in Ref 2).

In the present paper we wish to report upon investigations of the influences of concentration, temperature, and moisture content on the reactions of different carbohydrates in liquid hydrogen fluoride. Further studies were checking the possibilities for the synthesis of glucose derivatives in the same reaction medium. Finally, thermochemical results will be given concerning the action of gaseous hydrogen fluoride on lignocellulose, the residue of a dilute acid prehydrolysis of wood.

THE BEHAVIOR OF CARBOHYDRATES IN LIQUID HYDROGEN FLUORIDE

Concentration and Temperature Effects

It was shown previously[2-5] that the formation of reversion products from, e.g., cellulose can be favored or suppressed by appropriate variation of the concentration, temperature, and the work-up steps.

Our aim was to prepare oligomers with a low average degree of polymerization (DP) from cellulose, amylose, and starch for the purpose of subsequent derivatization, such oligomers being dextrins with an intact α-, resp., β-$(1 \rightarrow 4)$ linkage as well as reversion products. By the experiments we made in this respect the results of previous investigations[2] could roughly be confirmed. In a series of reactions the carbohydrate concentration and the reaction temperature were varied broadly, the reaction time being mostly 1 h. As a rule, the work-up was performed by adding diethyl ether to the reaction mixture, filtering, and neutralizing the aqueous solution of the ether precipitate with $CaCO_3$. After freeze-drying, analyses were made by HPLC, and the specific rotation data were collected.

As an example, in Figure 1 the HPLC diagram of the carbohydrate mixture (c) which was obtained from cellulose/HF at low concentration and temperature conditions is given and compared to those of glucose syrup* (a) and of a product (b) which had been obtained by complete degradation of cellulose to the monomeric form (α-glucosyl fluoride) and subsequent HF evaporation as an alternative work-up procedure.

*Commercial glucose syrup (synonymous with starch syrup, or maltodextrins) is manufactured by partial enzymatic or chemical hydrolysis of starch.

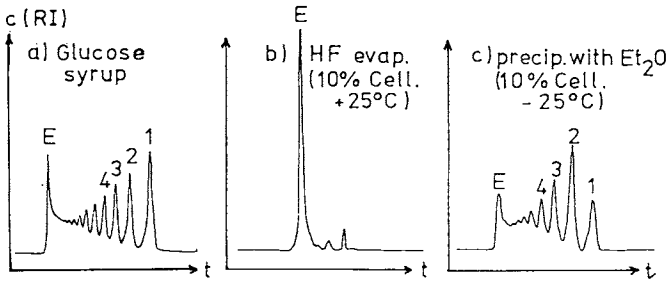


Fig. 1. HPLC analyses of saccharide mixtures prepared from cellulose/HF under different workup conditions (see Experimental) compared to glucose syrup.

As can be seen from the diagram (a), the sharpness of the individual peaks corresponds to the structural homogeneity of the maltodextrin molecules. In this respect there is a strong evidence for a similar uniformity of structure in our products derived from cellulose, as is illustrated in the diagram (c). The comparatively smaller portion of glucose contained in the (c) mixture is caused by losses due to the solubility of glucose in the precipitation medium (diethyl ether/HF 5:1 v/v). As a crude measure for the presence of low molecular weight saccharides, the peak height relation of DP 2 vs. DP *E* was evaluated from the data of each HPLC analysis (peak *E* characterizing the amount beyond the exclusion border of the separating column).

According to the literature,[6] specific rotation values below approx. +45°, afford evidence for the occurrence of cellulose oligomers with glycosidic β, 1 → 4 bonds. These values, in combination with the HPLC data, allowed us to ascertain the best conditions for the formation of cellodextrins more precisely than hitherto given in the literature. These conditions comprise a carbohydrate concentration of 10% b. w. in the HF medium, and a reaction temperature range from −15 to −25°C for the time of 1 h, followed by ether precipitation. Thus the DP 2/DP *E* range was found to be between 2.0 and 2.5, and the specific rotation α_D^{20} ($C = 10$, water) between +25 and +35°C. The yields ranged from 70 to 84% b. w. of the theoretical.

For comparison, Figure 1(b) shows the effect of the HF evaporation which in the course of the concentration enhancement leads to an almost complete reversion of the originally formed cleavage products. Results: DP 2/DP $E < 0.1$; $\alpha_D^{20} > 80$°C; yields, > 90% by weight of the theoretical.

Besides the specific rotation, the structure of the cellodextrins was further confirmed independently by preparation according to the literature[7] as well as by the ^{13}C-NMR data which are consistent with prior findings.[8] In Figure 2 the spectrum of a typical cellodextrin mixture is depicted. The characteristic signals at 105 ppm caused by the β-linked anomeric C-1 and the one at 81.5 ppm for a glycosylated C-4 prove the cellodextrin structure. Besides, both ^{13}C- and ^{1}H-NMR data indicate an approximately 10% content of 1,6-anhydroglucopyranose or of oligomers with a terminal 1,6-anhydroglucose unit (C-1 at 104.3 ppm, C-6 at 67.9 ppm). The doublet at 109.0 ppm with a coupling constant of $^{1}J = 221$ Hz is caused by the C-1 of α-glucopyranosyl fluoride.

In a number of parallel experiments under similar conditions with respect to temperature and concentration other starting materials like Cellunier F,

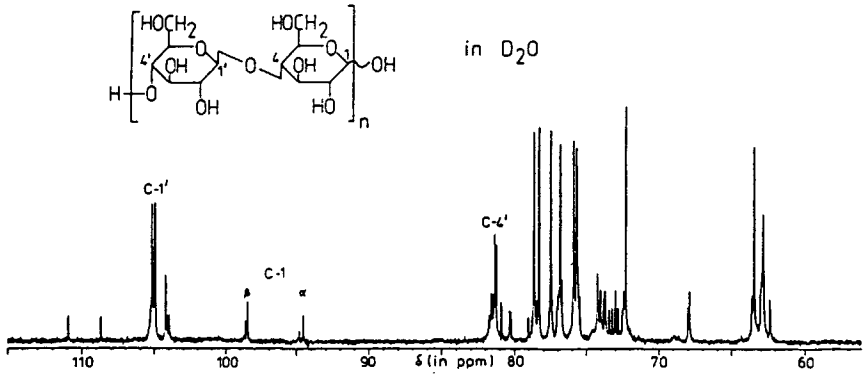


Fig. 2. ^{13}C-NMR spectrum (100.6 MHz, D_2O) of the cellodextrins prepared during 1 h in 10% concentration at $-15°$C.

Cellucot ES 5000, ALF, DYCW, Buckey V5, and Whatman CC-31 with DP values from 550 to 2500 were studied. It turned out that the structural composition of the products is not dependent on the DP of celluloses used.

The treatment of amylose under the cellodextrin conditions (e.g., 10%, $-25°$C) leads to a much faster cleavage of the glycosidic bonds, yielding mainly α-glucosyl fluoride. Therefore, this method is not applicable for the preparation of maltodextrins. Under those conditions, the reversion reaction seems to be of minor importance. However, in contrast to the cellulose behavior temperatures about $-5°$C give rise to a considerable formation of reversion products.

The Effect of Water Content

The results of Defaye et al.[2] had shown that glucose, cellulose, and starch, on reaction with HF and subsequent evaporation, give rise to the same linkage patterns. However, the molecular weight distribution of the glucose product is different from the two others as can be seen by gel permeation analysis (cf. Ref. 9). In Figure 3 the gel chromatogram curves of the reversion products derived from glucose and cellulose, resp., are given. The values of DP_{50} which are calculated from the diagram† differ significantly, namely by 15 monomer units. Further experiments revealed that this effect could be attributed to the formation of 1 eq of water during the reaction of glucose to α-glucosyl fluoride.

A GPC profile similar to Figure 3(a) can be achieved from cellulose and starch reversion products, too, on adding water to the HF reaction mixture or by use of moist starting material. In a few examples given in Table I, the effect of water formed in the reaction or of added water, resp., on the average degree of polymerization DP_{50}‡ is illustrated. This method, therefore, is suitable for the preparation of low molecular weight reversion products.

In contrast to these observations, the distribution pattern of the glycosidic linkages is apparently not affected by the water content. Professor P. E.

†DP_{50} is defined here as the value of DP just dividing the area under the graph in half.
‡See the preceding footnote.

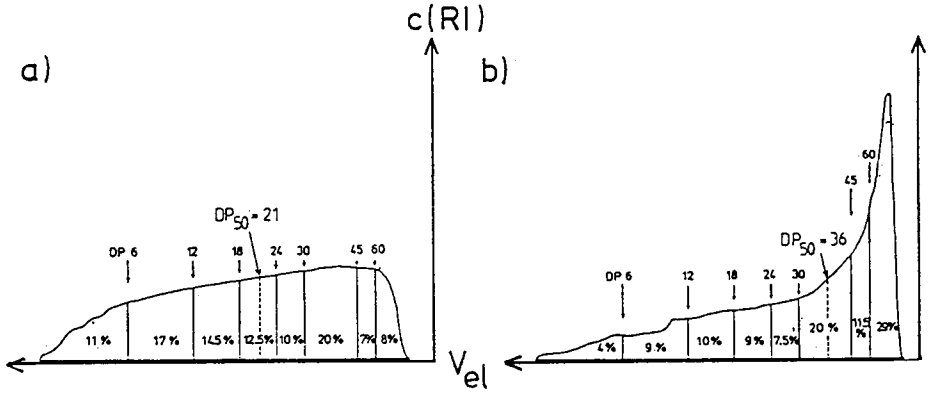


Fig. 3. GPCs showing the molecular weight distribution in the reversion products prepared from glucose (a) and cellulose (b). Conditions: see Experimental.

TABLE I
The Dependence of the DP_{50} on the Water Content of the Starting Material

Material	Cellulose		Starch		Glucose
Water content (%)	0	20	0	20	10
DP_{50}	36	14	28	12	21

TABLE II
Methylation Analysis Results[a] of Reversion Products Derived from Different Carbohydrates

Distribution of methyl groups	Glucose (%)	Cellulose (%)	Potato starch (%)
2,3,4,6-Tetra-*O*-Me	40	41	44
2,4,6-Tri-*O*-Me	10	10	11
3,4,6-Tri-*O*-Me	8	8	8
2,3,4-Tri-*O*-Me	21	22	20
2,3,6-Tri-*O*-Me	7	8	7
2,6-Di-*O*-Me	1	—	—
2,4-Di-*O*-Me	3	4	4
2,3- and 3,4-Di-*O*-Me	10[b]	6[c]	5[d]

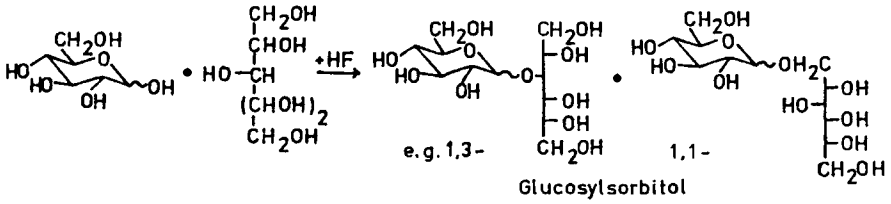
[a] P. E. Jansson, University of Stockholm.
[b] ratio 2,3–3,4 = approx. 1:1.
[c] ratio 2,3–3,4 = approx. 1:2.
[d] ratio 2,3–3,4 = approx. 1:2.

Jansson (University of Stockholm) kindly carried out methylation analyses of the reversion products derived from glucose, cellulose and starch, the results of which are summarized in Table II.

The Derivatization of Carbohydrates in Liquid Hydrogen Fluoride

The formation of carbohydrate reversion products in liquid hydrogen fluoride is due to the acid-catalyzed glycosylation of one molecule with the hydroxyl group of another molecule. This gave rise to the question of glyco-

sylating glucose in the presence of mono- or polyvalent alcohols. If 1 eq of a monovalent alcohol like methanol would be used the desired formation of methyl glucoside, for statistical reasons, should be unfavorable compared with the saccharide chain propagation. In order to suppress the latter and favor a distinct glycoside synthesis, either a great molar excess of the monovalent alcohol or the use of a penta- or hexavalent alcohol like, e.g., xylitol or sorbitol seemed to be necessary.



Scheme 2

Both conceptions were examined experimentally. After reaction of glucose with a 20-fold molar excess of methanol in HF, a product containing 99% of methyl glucoside was isolated according to proton resonance spectra and GLC. A sixfold molar excess of *n*-octanol, however, yielded a reversion product containing only a few *O*-glycosidically linked *n*-octyl groups, as was shown by ^{1}H-NMR and HPLC. By reaction of equimolar amounts of glucose and *n*-octanol liquid hydrogen fluoride the *n*-octyl glucopyranoside was not detectable any more (^{1}H-NMR, TLC). On the other hand, by treatment of glucose with sorbitol even in an equimolar ratio the product consisted of 49% of a mixture of the isomeric glucosyl sorbitols (cellobiitol, isomaltitol etc.), according to the HPLC analysis. Furthermore, 23.9% of oligo- and polysaccharides, 21.4% of sorbitol, and 1.8% of glucose were detected. This is consistent with a 57% incorporation of sorbitol into the saccharide molecules. When the sorbitol portion is lowered in the starting mixture, the free sorbitol in the product will be diminished too, and the relative extent of the sorbitol incorporation, adversely, enhanced. Thus, at an initial glucose/sorbitol ratio of 2:1 the percentage of free sorbitol in the product was 22.8% of the initial amount, at

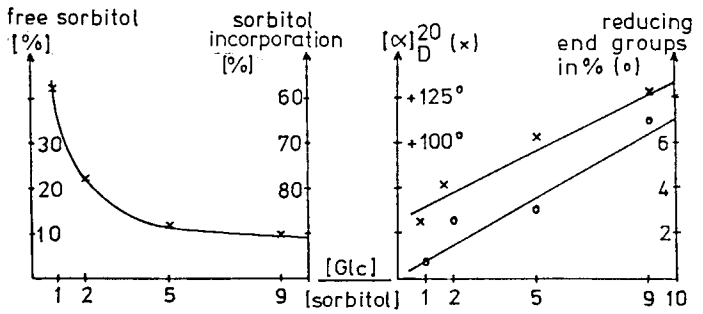
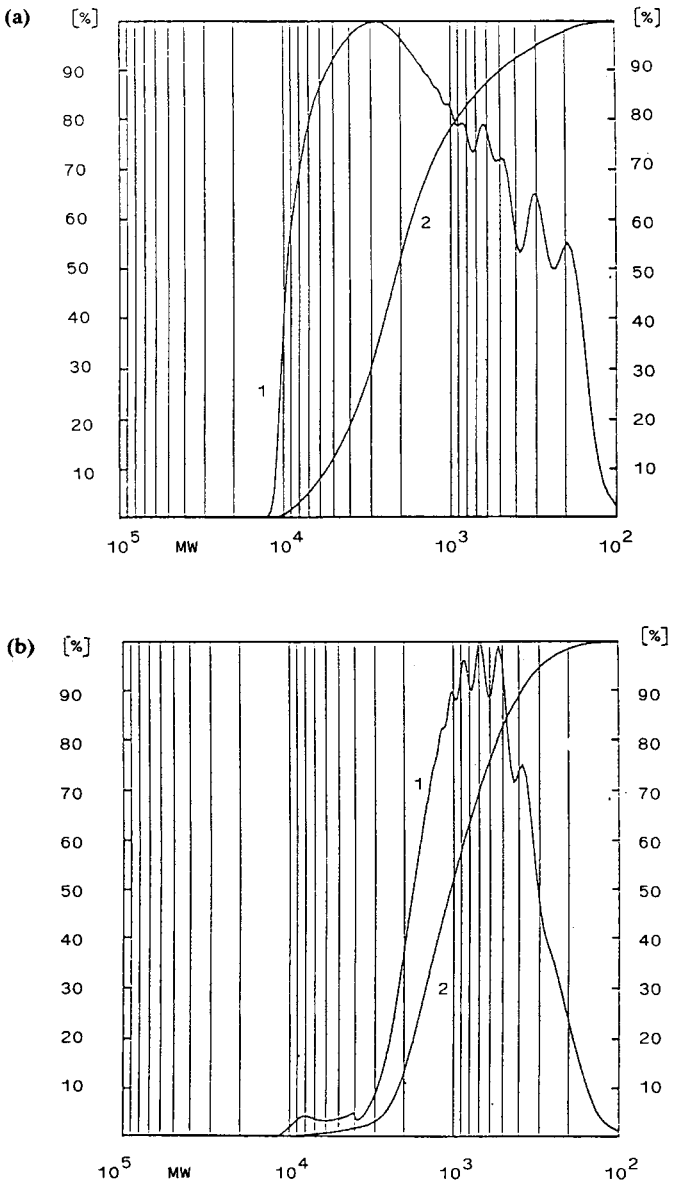


Fig. 4. Sorbitol incorporation and free sorbitol content in the product (a), as well as specific rotation values and content of reducing end groups (b), each as a function of the glucose/sorbitol initial ratio.

5:1 it was 12%, and at 9:1 only 10%. Correspondingly, the portion of incorporated sorbitol was enhanced [see Fig. 4(a) and Table V (Experimental)]. Figure 4(b) shows the dependence of further product properties on the variation of the sorbitol content in the starting material. Lowering of the latter causes an increase in reducing end groups (cf. Experimental) and also a significant one in the specific rotation values.



Figs. 5(a) and (b). Gel permeation chromatogram profiles of the reversion products prepared with a glucose/sorbitol ratio of 99:1 (a) and 5:1 (b). Curve 1: Plot of the relative area of slices below the original chromatogram curve (elution time for each slice: approx. 3.25 min; the maximum slice area found was set to 100%) vs. the log of molecular weight. Curve 2: Plot of the cumulated absolute slice area percentage vs. log of molecular weight.

From these results it can be concluded that even hexavalent alcohols cannot compete in reactivity with other glucose molecules for a glucosyl fluoride unit. However, the reduction of the incorporated material, as well as of the reducing end groups and of the specific rotation as a consequence of an enhanced initial sorbitol amount, point to a chain-terminating and molecular-weight-lowering influence of the sorbitol. This conclusion was confirmed, finally, by GPC analyses, the profiles of which are shown in Figures 5(a) and (b).

THE ENTHALPY OF SORPTION OF HYDROGEN FLUORIDE GAS ON SPRUCEWOOD LIGNOCELLULOSE: HEAT OF DESORPTION MEASUREMENTS

Wood Saccharification with Hydrogen Fluoride

A comparative study of the procedures known from the literature dealing with the acidic degradation of cellulose containing biomass reveals that the easiest acid recovery can be achieved by the use of anhydrous hydrogen fluoride. This advantage was already recognized more than 50 years ago,[1c] preponderating the necessity of a subsequent posthydrolysis of the degradation products in order to obtain fermentable glucose. A process using gaseous hydrogen fluoride was developed at that time by Fredenhagen, Helferich, and several scientists from IG Farben.[10]

In the course of a recent reexamination of this process at Hoechst AG, lignocellulose, i.e., the residue of a dilute sulfuric acid prehydrolysis of wood,[11] was used as a substrate.[12] This is in contrast to other recent investigations in which chemically unchanged biomass and liquid hydrogen fluoride are used.[2,5] Lignocellulose as the starting material leads to an advantageous handling of the reaction mixture and to a better overall yield of sugars from the "pre" and the "main" hydrolysis. In most cases, the HF sorption and desorption steps on lignocellulose were performed batchwise in rotating drums. Residual amounts of hydrogen fluoride were blown off in fluidized bed dryers. This was followed by an aqueous work-up and yielded oligomeric reversion products in an amount of 90% with respect to the substrate's cellulose content.

With respect to structure and composition, the products are very similar to those prepared at ambient temperatures from glucose, pure cellulose or starch and liquid HF; however, there are also differences concerning, e.g., a higher content of β-glycosidic bonds. The molecular weight distribution pattern is again very much dependent on the degree of moisture.

In addition to these studies exact thermochemical measurements were performed. The planning of a technical realization of the process required data of the caloric output and intake of the HF sorption and desorption, resp., which were measured with lignocellulose as the substrate.

The Isothermic HF Sorption

A water calorimeter was modified to fit for reactions in the gaseous–solid states. Into the stainless steel reaction vessel of this calorimeter containing 50 g of crushed and sieved sprucewood lignocellulose (granule size approx. 1 mm) HF gas was introduced from an evaporator under stirring. The gas stream was

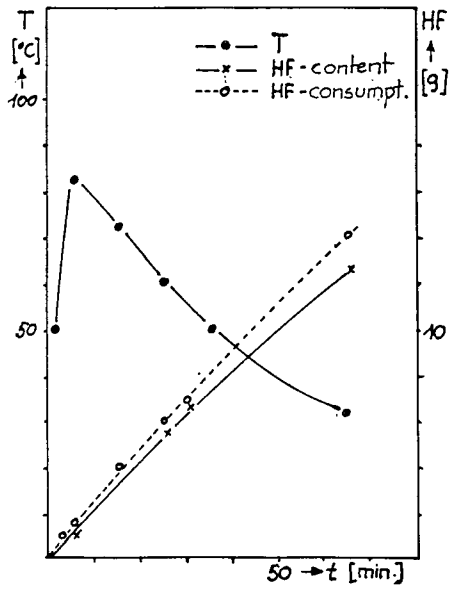


Fig. 6. Adiabatic sorption of HF gas mixed with air (10 L/h) onto 9 g of sprucewood lignocellulose in an insulated reactor.

regulated to provide a reaction as isothermical as possible (in the view of the difficult and slow heat transfer in that reaction system) and to avoid uncontrolled heat losses. Thus the isothermic heat of sorption was calculated to be 340 kcal or 1430 kJ/kg of the initially used hydrogen fluoride.[§]

The Adiabatic HF Sorption

In contrast to the sorption in the water calorimeter described above the practical sorption of HF gas on biomass is performed predominantly in an adiabatic process as a consequence of velocity, reactor size, and the above-mentioned poor heat conductivity in the reaction mixture. Thus, questions arose for the possibility of product damage by overheating, especially in the view of the high isothermic heat output result. In usual preparations, however, such overheating had never been observed. As a model, sorption experiments were carried out in an insulated polyethylene reactor, monitoring the increases of the temperature and the HF loading. In all experiments, the temperature rose only a little over 80 °C which was immediately followed by a decrease being almost as rapid as the increase. Remarkably, the course of the HF loading vs. time was not affected by the temperature changes (cf. Fig. 6).

Since the heat capacities of the lignocellulose present and the carrier gas passing through are rather low, the anomalous shape of the temperature curve obviously is due to the extraordinarily high heat consumption by the cleavage of the oligomeric $(HF)_x$ molecules in the gas phase. Between the boiling point and 70 °C the specific heat of gaseous hydrogen fluoride is culminating in a sharp peak at a 30-fold value compared with higher temperatures.[13] A great

[§]For carrying out the measurements and the interpretation we are grateful to Dr. Hannelore Zeininger, Applied Physics Department, Hoechst AG.

deal of the enthalpy of the isothermic sorption, therefore, is consumed by the hydrogen fluoride gas itself for its warming up, provided that it is present in sufficient amounts. The temperature profile during the sorption of gaseous hydrogen fluoride on biomass, accordingly, can be controlled to a certain extent, and it could be shown that the temperature maxima will not damage the product.

The Evaluation of the Desorption Enthalpy

The temperature dependence of the association of HF molecules in the gas phase has not yet been entirely elucidated.[14] As a consequence, problems arise on every assay for data concerning the energy consumption by the HF desorption from the lignocellulose/HF reaction mixture. We tried to approach the problem starting from two independent directions:

—first, by measuring and interpreting sorption–desorption equilibria;
— second, closer to a practical procedure, by performing the desorption in a current flow calorimeter by the aid of hot air.

In the first procedure, a gaseous HF/N_2 mixture having a constant and controllable composition was reacted with approx. 10 g of substrate in a small mantle-heated cylindric steel reactor which was mounted on a balance. When no changes were observed any longer in the weight and the temperature of the reaction mixture, and in the composition of the gas neither before nor behind the reactor, a state of equilibrium was reached; these data were registered (for details, see Experimental).

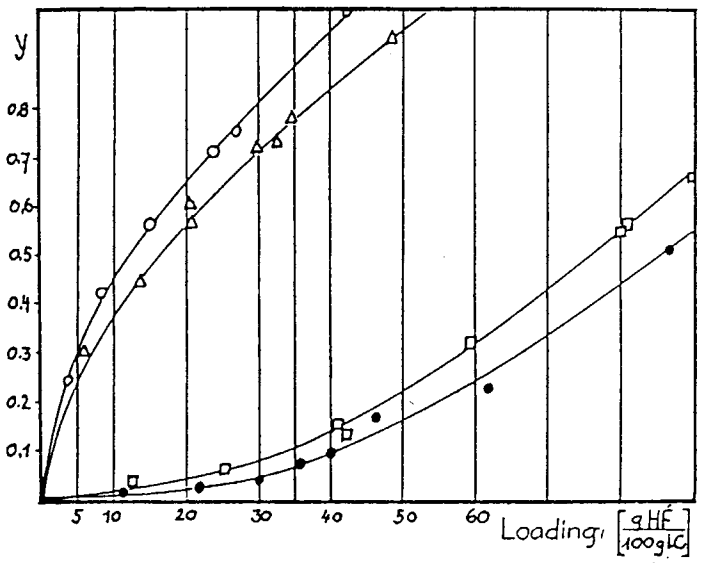


Fig. 7. Sorption/desorption equilibrium isotherms in the system HF_g/lignocellulose for different temperatures: (●) 30 °C; (□) 40 °C; (△) 60 °C; (○) 70 °C; plot of the HF mole fraction y in the gas mixture vs. the HF content x of the solid phase. The section points with the perpendiculars indicated the temperature dependence of y at given HF contents in the solid phase.

By varying the temperature, the equilibrium loading of the reaction mixture could be easily changed. This allowed several measurements with a single batch. Each composition weight ratio found in the gas mixture was converted into the molar fraction assuming, for reasons of simplicity, gaseous hydrogen fluoride to be dimeric at 30–40 °C but predominantly monomeric above 60 °C, and the molar fraction was plotted against the loading of the solid, as shown in Figure 7. Around 50 °C the data observed were quite scattered which points to a dissociation process going on at this temperature range.

From these results (by drawing perpendiculars on the x-axis), the temperature dependence of the equilibrium HF mole fraction y for different HF contents in the solids could be elucidated, as indicated in Figure 7. Two series of $\Delta \ln y$ values were calculated for one low and one high temperature range of $\Delta T = 10$ K, in order to introduce them into the Clausius–Clapeyron equation instead of $d \ln p$:

$$\frac{d \ln p}{d(1/T)} = -\frac{Q}{R}$$

In other words, we tried to treat the desorption of HF gas from the solid surface of lignocellulose like a vaporization process and then to calculate the enthalpy value Q. The measured and thereof calculated data are listed in Table III. The heat of desorption results for both temperature ranges in question are also shown graphically in Figure 8.

At high loadings there is obviously little difference between the desorption and the pure vaporization of HF; in contrast, as the desorption is continued, the energy consumption rises. This increase will commence earlier in the lower temperature range which is consistent with the assumption that in this range dimeric molecules are desorbed predominantly. The maximum value, which is to be expected when the loading is approaching zero, could not be determined exactly.

From the plots of Figure 8 the total energy requirement for a whole desorption process can be estimated only roughly. Therefore, an alternative procedure was developed which is closer to reality. Here lignocellulose charged with HF (100:60 b. w.) was treated with hot air under well-defined conditions in a stainless steel flow tube of 250 mL capacity. The gas inlet and outlet temperatures T_{in} and T_{out} were monitored, the HF evolved was analyzed continuously by an on-line titration and the passing air volume V was measured by a gas meter. Thus, the heat flow Q_{HF} could be calculated applying the equation

$$Q_{HF} = (T_{in} - T_{out}) \cdot V \cdot \rho \cdot C_P$$

after registering T_{in} and T_{out} every 3 min and summing up the partial Q_{HF} results. As the amount of air always largely exceeded that of the desorbed hydrogen fluoride, the influence of the latter on the density ρ and the specific heat C_P could be neglected. The temperature-dependent values of ρ and C_P are listed in handbooks. All experiments were terminated after approx. 50 min. By using HF-free lignocellulose under constant conditions, the caloric blind

TABLE III
Data Characterizing the Sorption/Desorption Equilibria and Correspondingly Calculated Values for the Heat of Desorption in the System HF_g/Lignocellulose

Loading (g of HF on 100 g of lignocell.)	Temp (° C)	Assumed mol wt of the $(HF)_x$	Molar fraction of the HF in the gas mixture	Heat of desorption (kJ/mol (HF)x)	(kJ/20 g HF)
5	60	20	0.24	26.8	26.8
	70	20	0.32		
10	60	20	0.38	15.7	15.7
	70	20	0.45		
20	30	40	0.02	52.2	26.1
	40	40	0.04		
	60	20	0.56	12.0	12.0
	70	20	0.64		
30	30	40	0.04	42.3	21.2
	40	40	0.07		
	60	20	0.72	11.1	11.1
	70	20	0.81		
35	30	40	0.07	34.0	17.0
	40	40	0.11		
	60	20	0.78	10.6	10.6
	70	20	0.90		
40	30	40	0.10	26.5	13.2
	40	40	0.14		
	60	20	0.85	10.2	10.2
	70	20	0.95		
50	30	40	0.16	24.2	12.1
	40	40	0.22		
60	30	40	0.24	21.9	11.0
	40	40	0.32		
70	30	40	0.33	18.9	9.5
	40	40	0.43		
80	30	40	0.43	18.1	9.1
	40	40	0.55		
90	30	40	0.55	15.9	7.9
	40	40	0.67		
		For comparison:			
		heat of vaporization of liquid HF at		35° C	6.8
		(cf. Ref. 13c)		65° C	9.4
				75° C	9.9

value Q_{blv} of the apparatus was determined and substracted from the Q_{HF} value, as demonstrated in Table IV.

The average value for the heat of desorption (initial lignocellulose/HF ratio 100:60) therefore is

Q_{Des} = 868.3 kJ or 207.4 kcal/kg of HF and 17.4 kg or 4.2 kcal/20 g of HF, resp.

The high level of the caloric blind value and the fact that in every experiment only a portion of the total HF present was desorbed by the aid of a great excess of the carrier gas, give rise to an estimated error of at least ±10%;

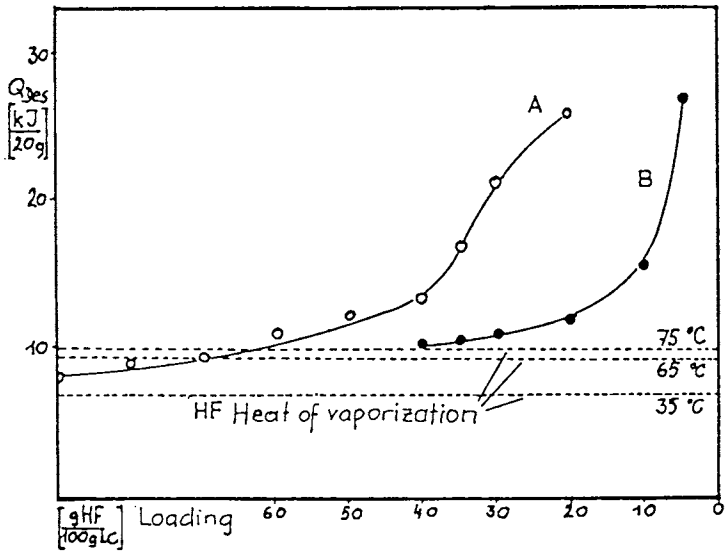


Fig. 8. Heat of desorption in the HF_g/lignocellulose system as a function of the HF loading on the solids, for the temperature ranges of 30–40 °C (A) and 60–70 °C (B).

TABLE IV
HF Desorption from Sprucewood Lignocellulose in a Current Flow Calorimeter

Expt no.	Amount of HF desorbed (g)	Q_{HF} (cal)	Q_{blv} (cal)	$Q_{HF} - Q_{blv}$ (cal)	Q_{Des} (kJ/kg HF)
1	7.62	8963	7425	1538	845
2	9.28	9472	7471	2001	903
3	9.60	10631	8664	1967	858

nevertheless, the result found here is consistent with the picture shown in Figure 8.

EXPERIMENTAL

Physical Measurements

HPLC analyses** were performed on a Spectra Physics 8100 model which was combined with the Spectra Physics 6040 differential refractometer. Two columns were used on-line: first, an Aminex HPX-85C column, then, for the separation itself, the Bio-Rad HPX-42C column (300 × 7.8 mm). Working pressure: 20–35 bars; eluent, aqua bidest. of 85 °C, which had been degassed by a helium current. Automatic injection of 10 μL of a 5% solution at a flow rate of 0.5 mL/min.

The NMR spectra were taken on a Bruker WM 400 spectrometer. Sodium trimethylsilyl propionyl sulfonate was used as a standard for the D_2O solutions.

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The conditions for the gel permeation chromatographic separations[††] were adopted from the work of John et al.[9]: Bio-Rad Biogel P 6 (200–400 mesh) in a 100 × 2.6 cm glass column, temp. 45 °C. Demineralized and degassed water was used as eluent in descending flow with a rate of 300 mL/h, and every 1 mL dose contained 50–100 mg of carbohydrate. In part, the detection was achieved by an RI detector from Waters Comp., later, the procedure was improved by the use of the Spectra Physics 6040 differential refractometer in combination with the Spectra Physics 4200 computing integrator (GPC + ENH Program). At first the calibration was performed with partially enzyme-hydrolyzed pullulan (maltotriose units containing polysaccharide). Later and more accurately, an autocalibration was carried out by aid of the computing integrator, assuming, e.g., the first peak in Figure 5(a) to be molecular weight 180, the second 342, the third 504, etc.

The specific rotations were determined in aqueous solution on a Perkin-Elmer 141 polarimeter (tube length 10 cm, concentration 10%, temp 20 °C, Na-D-line).

The reducing end groups were determined by the method described by Hostettler[15] consisting in the reduction of 3,5-dinitrosalicylic acid.

CHEMICAL PROCEDURES

The cleavage of cellulose and the isolation of the oligomeric reversion products (cf. Table I)

Approximately 50 g of hydrogen fluoride were condensed in a polyethylene vessel immersed in a freezing bath of −10 °C, and weighed exactly afterwards. Within the temperature range between −10 and 0 °C the appropriate amount of cellulose powder (Cellulose Type S, Riedel de Haen Comp.) was added with magnetic stirring. After no more than 5 min the vessel was placed into a bath of the desired temperature and kept there for 1 h. Then 250–300 mL of precooled diethyl ether (−60 °C) were added, and the liquid was decanted cautiously. This procedure was repeated twice, followed by filtration of the remaining precipitate through a polyethylene membrane and washing with ether. The raw material was weighed, and then dissolved in water. The aqueous solution was neutralized with excess calcium carbonate, filtered, and freeze-dried to yield a colorless fluffy powder.

Reactions of Glucose with Sorbitol in Liquid Hydrogen Fluoride

Glucose and sorbitol in the amounts given in Table V were dissolved at 0 °C in liquid hydrogen fluoride which had been placed in a PTFE distillation apparatus. This 30% saccharide solution was stirred magnetically for 1 h at 20 °C; then, upon warming to 50–60 °C and stirring the hydrogen fluoride was distilled off, during which time the pressure was reduced slowly. After 1.5–2.5 h, 90% of the hydrogen fluoride had been removed which yielded between 145 and 160 g of a transparent and only slightly colored syrup. This product was dissolved in 300 mL of water, neutralized with solid calcium carbonate, centrifuged, and filtered by the aid of celite. The clear solution was evaporated

[††]See the preceding footnote.

TABLE V
Reaction of Glucose with Sorbitol in Liquid Hydrogen Fluoride

	Glucose/sorbitol ratio (w/w)	1:1	2:1	5:1	10:1
Starting mixture	HF amount (g)	193	195	93	314
	Glucose (g)	41.4	55.7	33.6	121.1
	Sorbitol (g)	41.4	27.9	6.5	13.5
Product	Yield (% b. w.)	78.1	76.6	84.3	83.2
	Spec. rotation $[\alpha]_D^{20}$	+56.7°	+77.1°	+102.2°	+128.1°
	Reducing end groups (mol 96%, of of the amount of monomer units)	0.7	2.6	3.1	7.1

to approx. 200 mL and freeze-dried overnight, which yielded a colorless amorphous product the hygroscopic properties of which increased with enhanced sorbitol content. Further information is given in Table V.

The reactions of glucose with the univalent alcohols methanol and *n*-octanol were carried out in an analogous manner in the same apparatus. The corresponding glycosides were identified or ruled out by comparison with authentic samples in the GLC analysis (after silylation), in the proton resonance spectra or TLC evaluation (silica gel, methylene chloride/methanol 10:1).

The Determination of the Sorption / Desorption Equilibria in the System Lignocellulose / HF

Gaseous hydrogen fluoride was taken from a gently heated steel cylinder, its flow rate being measured by a diaphragm flow meter. This HF current was mixed with a nitrogen current having a defined flow rate (cf. Ref. 16) and introduced into the substrate-filled reactor. This device was shaped as a mantled cylinder of 5 cm in length and 3 cm diameter equipped with penetrated rubber stoppers on both sides. The gas mixture evolved at the opposite end was analyzed on-line by determining the HF continuously in a KOH titration apparatus and measuring the portion of carrier nitrogen by a gas meter. To analyze the initial gas mixture by the same assembly, a bypass was installed. For the permanent control of the HF content in substrate, the reactor was mounted on a balance as forcelessly as possible. The substrate had been pretreated with HF independently in another flask before introduction into the reactor in order to prevent faults due to shrinkage. The heating mantle of the reactor was connected to an oil circulating thermostatic heater. At a given gas composition and substrate temperature the data characterizing the state of equilibrium were recorded after the balance reading had become constant.

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