Solvolysis of a Single Lignocellulose Wafer by Anhydrous Hydrogen Fluoride (HF) Vapor

Effect of Temperature on HF Adsorption, Glucose Production Rate, and Reversion Kinetics

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ABSTRACT

The solvolysis of a single lignocellulose wafer by anhydrous HF vapor at 1.0 atm was studied by exploring the effect of temperature (30 to 80°C) on (1) HF adsorption and desorption, (2) reaction rate and glucose yield, and (3) glucosyl fluoride repolymerization. All three processes are coupled, and 100% HF vapor temperature is the key process variable. The HF loading (g HF adsorbed/g-lignocellulose) decreased with increasing HF vapor temperature (1.42 g HF/g-lignocellulose at 31°C, 0.382 g HF/g lignocellulose at 60°C), indicating physical adsorption. Adsorbed HF was the limiting reagent for cellulose solvolysis: 0.4 g HF/g lignocellulose was required for saturation of hydroxyl groups and solvolysis of the glycosidic linkages. The extent of glucosyl fluoride repolymerization, as measured by HPLC-oligosaccharide profiling, increased with increasing HF vapor temperature. After posthydrolysis of water-soluble reaction products, glucose yields averaged 94% of theoretical.

Index Entries: Hydrogen fluoride; solvolysis; lignocellulose; adsorption; kinetics.

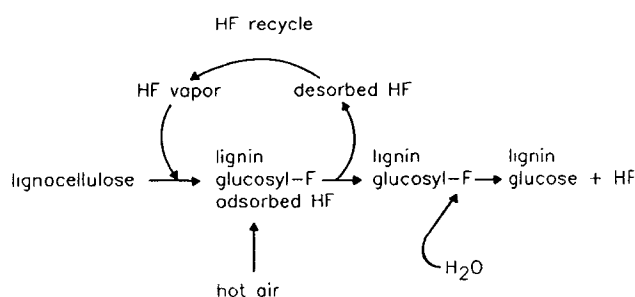*Author to whom all correspondence and reprint requests should be addressed.

HF recycle

HF vapor   desorbed HF

lignin   lignin   lignin
lignocellulose ———→ glucosyl—F ——→ glucosyl—F—→ glucose + HF
                  adsorbed HF

H_2O

hot air

Fig. 1.   Basic concept for vapor-phase HF solvolysis of lignocellulose.

INTRODUCTION

The steadily-decreasing supplies of nonrenewable petroleum resources increases the need to develop processes to efficiently convert renewable and abundant lignocellulosic biomass to useful chemicals and liquid fuels. A novel process worthy of consideration is solvolysis of lignocellulose by *anhydrous* Hydrogen Fluoride (HF) vapor. This process produces fermentable sugars and a residual lignin byproduct. The sugars can be biologically processed to a spectrum of useful products, including alcohols, ketones, and organic acids.

The vapor-phase HF solvolysis of lignocellulose offers high sugar yields, short reaction times at ambient processing conditions, and potential for simple and efficient recovery/recycle of HF, typically +99% (1–7). The basic concept of the vapor-phase HF solvolysis of lignocellulose is illustrated in Fig. 1. The process has three major stages

1. Physical adsorption of HF vapor onto lignocellulose and solvolysis of cellulose to glucosyl fluoride by adsorbed HF;
2. Desorption and recovery of adsorbed HF from the HF-reacted solid; and
3. Separation of glucosyl fluoride from residual lignin and hydrolysis of glucosyl fluoride and water-soluble oligomers to glucose.

The adsorption/reaction stage is the unique feature of the process. HF vapor molecules first diffuse into the porous lignocellulosic matrix. The HF molecules disrupt the para-crystalline matrix of the cellulose microfibril by displacing OH—OH hydrogen bonds with stronger HO—HF hydrogen bonds, as schematically illustrated in Fig. 2. In the HF-solvated state, the cellulose chains are free to undergo the conformational changes necessary
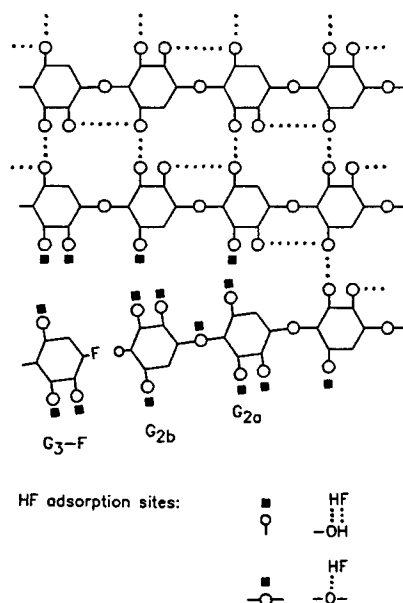
Fig. 2.   Solvolysis of the cellulose microfibril by adsorbed HF.

for solvolytic cleavage of the β-1,4 glycosidic linkage joining the glucan units.

The vapor-phase HF solvolysis of wood and agricultural residues has been studied on the pilot-scale by Husain, (1), Ostrovski et al. (2,3), Franz et al. (4,5), Reffstrup (6), and Bentsen (7), using semi-batch or continuous-flow reactors. However, the fundamental adsorption and reaction processes of the vapor-phase HF solvolysis of lignocellulose are not well known, especially with respect to HF adsorption/desorption thermodynamics, reaction kinetics, and heat/mass transport. Recently, Rorrer et al. (8–11) and Mohring et al. (12) have worked to characterize these fundamental adsorption/reaction processes.

The objective of this investigation is to explore the effect of 100% HF vapor temperature on three processes that occur simultaneously during the solvolysis of lignocellulose by anhydrous HF vapor: (1) HF adsorption, (2) solvolysis of cellulose to glucosyl fluoride by adsorbed HF, and (3) repolymerization of glucosyl fluoride to short-chain oligomers. The experimental design focuses on the reaction of a single "prehydrolyzed wood" (lignocellulose) wafer with an anhydrous, 100% HF vapor stream at 1.0 atm total pressure, and temperature of 30 to 80°C. The results of this investigation demonstrate that all three processes are coupled, and that HF vapor temperature is the key process variable that controls these processes.

MATERIALS AND METHODS

Lignocellulose Substrate

"Prehydrolyzed" wood wafers served as the model lignocellulose substrate. Preparation of this substrate is overviewed below.

Roughly-chipped Bigtooth Aspen wood (*Populus grandidentata,* Michx), was microtomed with the grain of the wood into shavings of 0.4 mm thickness. The shavings were then cut into wafers of 1.0 cm/side. The wafers were mildly refluxed in 2 *N* trifluoroacetic acid (TFA) at 100 °C for 4 h in order to solubilize the hemicellulose fraction by selective hydrolysis, and to remove extractives. The "prehydrolyzed" wood wafers were washed thoroughly with distilled water and dried at 100 °C (12 mg dry wt). The prehydrolyze wood, or "lignocellulose," was composed of 75% glucan, 22% lignin, and 3% residual xylan on a dry-wt basis.

Gravimetric HF Adsorption/Desorption

A novel, milligram-scale microbalance/reactor described in detail by Rorrer et al. (9) and Mohring et al. (12) was used to measure the *in situ* gravimetric uptake of HF vapor onto a single lignocellulose chip as a function of time and HF vapor conditions (flowrate, temperature, HF partial pressure).

Vapor-Phase HF Solvolysis Reactor

A novel, milligram-scale reactor described in detail by Rorrer et al. (9,11) inserted a single lignocellulose wafer into a HF vapor stream of controlled conditions (flowrate, temperature, HF partial pressure) for a given reaction time, retrieved the HF-reacted wafer from the reactor, and then rapidly quenched the reaction by depositing the HF-reacted wafer into 5.0 mL water.

The water-soluble reaction products were mildly hydrolyzed in 2 *N* TFA at 121 °C for 1 h in order to convert water-soluble oligomers to glucose. The glucose yield was quantified by High-Performance Liquid Chromatography (HPLC), using a Bio-Rad HPX-87P monosaccharide analysis column (analysis conditions: 0.6 mL/min HPLC-grade H_2O mobile phase, 85 °C column temperature, differential refractive index (RI) detection). The glucose yield (corrected for hydration of glucosyl fluoride and water-soluble oligomers) was defined as the grams of glucose in the water-soluble reaction products after posthydrolysis per gram of dry lignocellulose (g glucose/g lignocellulose). The glucose yield served as an assay for solvolysis of cellulose to glucosyl fluoride. By reacting a series of single lignocellulose wafers at different times at a fixed set of HF vapor conditions, glucose yield vs time curves as a function of HF vapor stream conditions were generated.
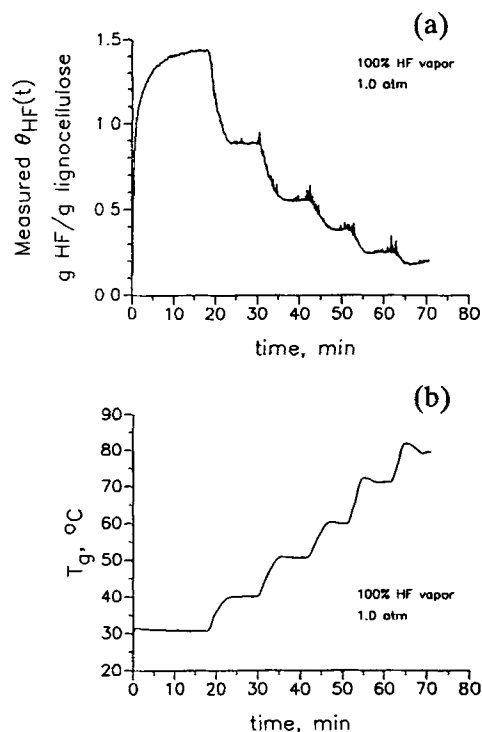
Fig. 3. HF adsorption/desorption data for the solvolysis of a single prehydrolyzed wood chip by a 100% HF vapor stream at 1.0 atm. (a) HF adsorption/desorption profile, θ_{HF} vs t; (b) 100% HF vapor stream temperature vs time profile, T_g vs t, used to set the HF adsorption/desorption profile.

RESULTS AND DISCUSSION

The objective of this investigation was to explore the effect of 100% HF vapor stream temperature on (1) the HF adsorption/desorption profile, (2) reaction rate and glucose yield, and (3) glucosyl fluoride repolymerization and the oligosaccharide product distribution.

HF Adsorption/Desorption Profile

HF loading vs time data from a typical adsorption/desorption experiment are presented in Fig. 3a. In this experiment, a 100% HF vapor flow (0.1 g HF/cm²/min) at 1.0 atm was continuously maintained over the sample during the HF adsorption and desorption steps. The 100% HF vapor stream temperature vs time profile (T_g vs t) used to set the HF loading vs time profile (θ_{HF} vs t) is given in Fig. 3b. The HF loading (θ_{HF}) is defined as

$$\theta_{HF} = \text{g HF adsorbed/g of lignocellulose.}$$

Table 1
Effect of HF Vapor Stream Temperature (T_g)
on Equilibrium HF Loading (θ_e) and Maximum Glucose Yield

T_g	θ_e				Maximum Glucose Yield	
			Experiment			Eqn. [1]
°C	g HF/g[a]	g/g[b]	+/- 1s	% theoretical		g/g[b]
31	1.420	0.786	+/-0.015	94.7	+/-1.8	0.830
41	0.866	0.774	+/-0.025	93.3	+/-3.0	0.830
52	0.519	0.778	+/-0.008	93.7	+/-1.0	0.830
60	0.382	0.784	+/-0.026	94.5	+/-3.1	0.830
68	0.297	0.696	+/-0.024	83.9	+/-2.9	0.669
80	0.181	0.416	+/-0.069	50.1	+/-8.3	0.406

[a] g HF adsorbed/g-lignocellulose
[b] g glucose/g-lignocellulose

The HF adsorption/desorption experiment was performed in two steps. In step 1, 100% HF vapor at 31°C was contacted with a single, dry prehydrolyzed wood wafer. HF adsorbed onto the lignocellulose chip, and the adsorbed HF reacted with the cellulose fraction to form glucosyl fluoride. The gravimetric uptake of HF onto the prehydrolyzed wood chip was measured as a function of time until an equilibrium HF loading (θ_e) was established at 31°C. In step 2, the 100% HF vapor stream temperature was increased to 40°C. A fraction of the HF physically adsorbed on the HF-reacted wafer desorbed from the wafer until a new, lower equilibrium HF loading was established at 40°C. The 100% HF vapor temperature was ramped in 10°C increments (5 min hold time) to a final temperature of 80°C. The sample wt (adsorbed HF+HF-reacted lignocellulose), HF vapor temperature, and HF vapor flowrate, were measured continuously by computer.

The equilibrium HF loading (θ_e) at a given 100% HF vapor temperature (T_g) was determined by averaging plateau $\theta_{HF}(t)$ data over time at constant T_g (Table 1). As shown in Table 1, θ_e decreased with increasing HF vapor temperature away from the normal boiling point of HF (19.54°C), indicative of physical adsorption.

The HF loading is the sum of five processes: (1) physical adsorption of HF on the hydroxyl (—OH) groups and glycosidic linkages (—O—) of cellulose, (2) HF consumed by solvolysis of cellulose and hemicellulose to glucosyl fluoride, (3) physical adsorption of HF on hydroxyl groups and ether linkages on lignin, (4) multilayer adsorption of HF onto existing HF-adsorbed sites, and (5) pore-condensation of HF vapor into the micropores

within secondary cell walls of the lignocellulosic matrix. By stochiometric considerations (*see* Eqs. [1] and [2]), a HF loading of about 0.4 g HF/g wood by processes 1 and 2 is required for complete saturation of —OH groups and solvolytic cleavage of cellulose to glucosyl fluoride. In general, the magnitude of the adsorption energy decreases from processes 1 and 2 (highest) to process 5 (lowest). Correspondingly, the ease of HF desorption increases from processes 1 and 2 to process 5. The adsorption of HF vapor onto the lignocellulosic matrix is an exothermic process, whereas the desorption of adsorbed HF from the HF-reacted solid is an endothermic process. Heat of adsorption vs HF loading data for the vapor-phase HF solvolysis of wood were determined previously (*4,5,12*) by applying the Clausius-Clapeyron Equation to equilibrium HF loading vs HF partial pressure isotherm data at temperatures from 30 to 80°C.

Reaction Rate and Glucose Yield

Effect of 100% HF Vapor Flowrate

The reaction of HF vapor with a single lignocellulose wafer was subject to external mass-transfer resistances. Since this reaction generates only solid glucosyl fluoride products that reside on an intact and porous lignin framework, in principle, no gas-phase external mass-transfer resistances can exist for the reaction of 100% HF vapor (no diluent) with lignocellulose, because no HF vapor concentration gradients can exist between the bulk phase and the lignocellulose wafer surface. However, the void volume of the very porous (ca. 3 mL/g) prehydrolyzed wafer was filled with air. When the 100% HF vapor flowed over the wafer, air diffused out of the wafer and created a film around the wafer through which incoming HF vapor had to diffuse, until all the air diffused out. The effect of HF vapor flowrate on the glucose yield vs time curve at $T_g = 31°C$ is shown in Fig. 4. The mass flowmeter metering HF vapor flow was calibrated so that 1.00 slpm (std. liters per min) equaled 0.21 g HF/cm²/min. An HF vapor flowrate (G_{HF}) of 0.42 g HF/cm²/min was sufficient to minimize external mass transfer resistances for a lignocellulose wafer thickness of 0.4 mm.

Effect of 100% HF Vapor Temperature

Glucose yield vs time profiles obtained from the reaction of single, dry, prehydrolyzed wood chips with HF 100% vapor at 1.0 atm and temperatures (T_g) of 31°C to 68°C are presented in Fig. 5. These data were obtained under a 100% HF vapor mass flowrate ($G_{HF} = 0.42$ g HF/cm²/min), where mass-transfer resistances were minimized. The sigmoidal shape of the glucose yield vs time curve is indicative of the sequential adsorption-reaction process.

The glucose yield vs time profile decreased with increasing HF vapor stream temperature. To explain this behavior, consider that the cellulose solvolysis rate is dependent on (1) glucan concentration, and (2) HF loading on the lignocellulosic matrix, and (3) reaction temperature. As the
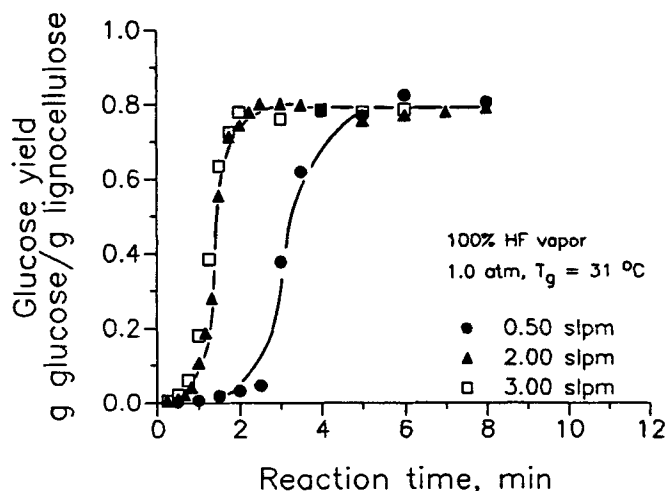
Fig. 4.   Vapor-phase HF solvolysis of a single prehydrolyzed wood wafer: effect of 100% HF vapor stream flowrate on the glucose yields vs time profile at $T_g = 31°C$. Note: mass flowmeter for HF vapor calibrated so that 1.00 slpm equaled 0.21 g $HF/cm^2/min$ in the reactor (linear response).
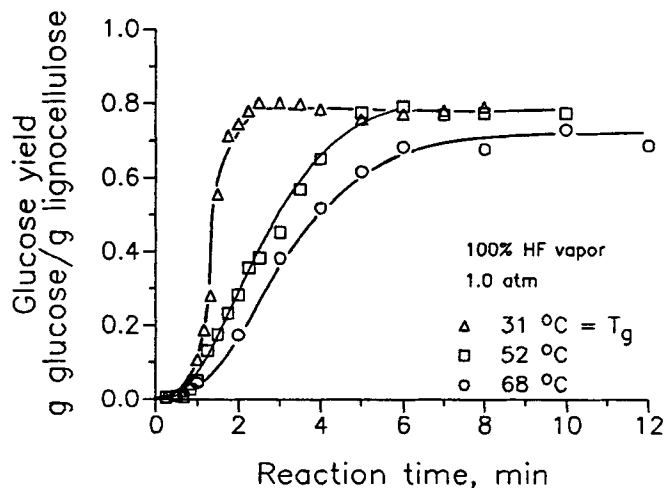

Fig. 5.   Vapor-phase HF solvolysis of a single prehydrolyzed wood wafer: effect of 100% HF vapor stream temperature ($T_g = 31°C$, 52°C, 68°C) on the glucose yield vs time profile.

reaction temperature increases, the intrinsic rate constant for cellulose solvolysis increases, but the HF loading (θ_e) on the lignocellulosic matrix that the cellulose perceives for the solvolysis decreases (i.e., T ↑ k ↑ θ_e ↓). Thus, the thermodynamics of HF physical adsorption and Arrhenius kinetics of cellulose solvolysis are coupled, and work in opposing directions with increasing temperature. This coupling determines the overall decrease of the glucose yield vs time profile with increasing HF vapor temperature.
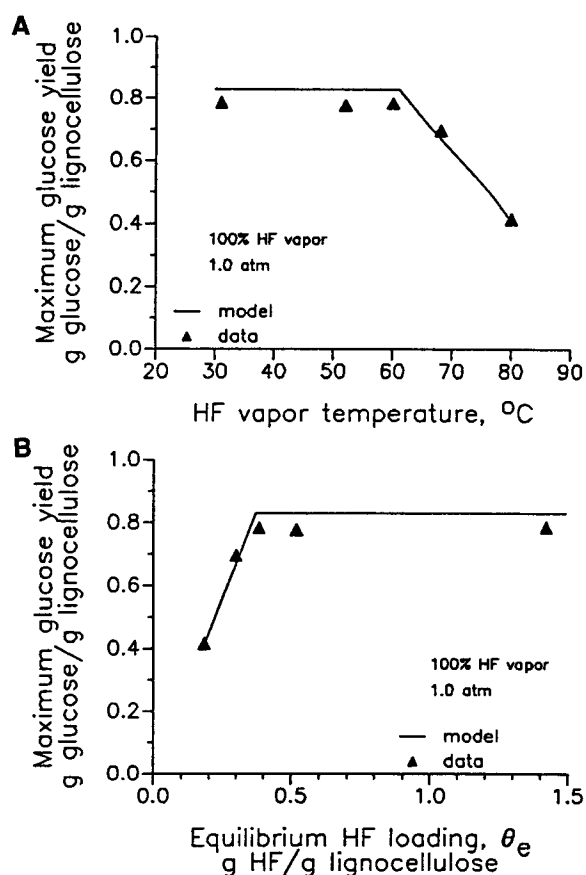
Fig. 6. Vapor-phase HF solvolysis of prehydrolyzed wood: (a) effect of 100% HF vapor temperature (T_g) on the maximum average glucose yield attainable from the water-soluble products (after posthydrolysis); (b) effect of equilibrium HF loading (θ_e) on the maximum average glucose yield. The model line was calculated using Eq. (1).

At 100% HF vapor temperatures greater than 60°C, the maximum attainable glucose yield was also dependent on the 100% HF vapor stream temperature, as shown in Fig. 6a. Since the dependence of equilibrium HF loading (θ_e) on 100% HF vapor temperature (T_g) was known from Fig. 3 and Table 1, the dependence of maximum attainable glucose yield on the θ_e was determined. The results are shown in Fig. 6b and Table 1. In Fig. 6, the theoretical dependence of maximum glucose yield on θ_e was calculated by

$$[G'_o] = \begin{cases} [G_o] \, \theta_e(T_g)/\theta_{min} & \text{if } \theta_e < \theta_{min} \\ [G_o] & \text{if } \theta_e \geq \theta_{min} \end{cases} \tag{1}$$

where $[G'_o]$ is the maximum glucose yield at a given equilibrium HF loading (θ_e), $[G_o]$ is the total glucan concentration in prehydrolyzed wood

(4.61 mmol glucan/g lignocellulose, or 0.83 g glucose/g lignocellulose), and θ_{min} is the theoretical minimum HF loading for complete solvolysis of the cellulose fraction in lignocellulose. The theoretical minimum HF loading, θ_{min}, was calculated by

$$\theta_{min} = 4\, M_{w,HF}\, [G_o] = 0.369 \text{ g HF/g-lignocellulose} \qquad (2)$$

where $M_{w,HF}$ is the mol wt of HF (20 g/mol). The factor 4 in Eq. (2) is the number of HF molecules per glucan unit required to solvate glucan in crystalline cellulose to glucosyl fluoride: 3 HF molecules to hydrogen bond with each of the 3—OH groups on the glucan unit (3 HO—HF complexes per glucan unit), and 1 HF molecule to solvolytically cleave the β-1,4-O-glycosidic linkage and form glucosyl fluoride.

Equation (1) predicts the maximum attainable glucose yield when the HF adsorbed on the lignocellulosic matrix is not sufficient to insure a stoichiometric reaction with cellulose. As demonstrated in Fig. 6, the simple model predicts the observed data.

The maximum glucose yield in the water-soluble reaction products (after posthydrolysis) averaged 0.78 g glucose/g lignocellulose. Since the maximum theoretical glucose yield is 0.83 g glucose/g lignocellulose, glucose recoveries averaged 94% of theoretical.

Glucose Fluoride Repolymerization and Sugar-Oligomer Product Distribution

It is well established that glucose or polysaccharides dissolved in anhydrous liquid HF form glucosyl fluorides, which subsequently repolymerize to short-chain, water-soluble oligosaccharides possessing a spectrum of sizes and glycosidic linkage composition (*13–17*). The HF solvolysis of cellulose to glucosyl fluoride and the subsequent repolymerization of glucosyl fluoride to oligomers (a process called reversion) is viewed mechanistically in Fig. 7. Note in Fig. 7 that the fluorine group on glucosyl fluoride attacks free —OH groups on other sugars, and by a condensation reaction, creates a stable glycosidic linkage and regenerates HF. A competing reaction is the hydrolysis of glucosyl fluoride to glucose, which also regenerates HF.

The extent of glucosyl fluoride repolymerization during the vapor-phase HF solvolysis of a single lignocellulose wafer was quantified by measuring the water-soluble monomer-oligomer product distribution as a function of time and 100% HF vapor temperature.

Analysis Technique

In order to freeze the monomer-oligomer distribution at a given reaction time and 100% HF vapor temperature, the HF vapor/lignocellulose reaction was "quenched" by dropping the HF-reacted lignocellulose wafer (ca. 12 mg) into 5.0 mL of water. Adsorbed HF and water-soluble

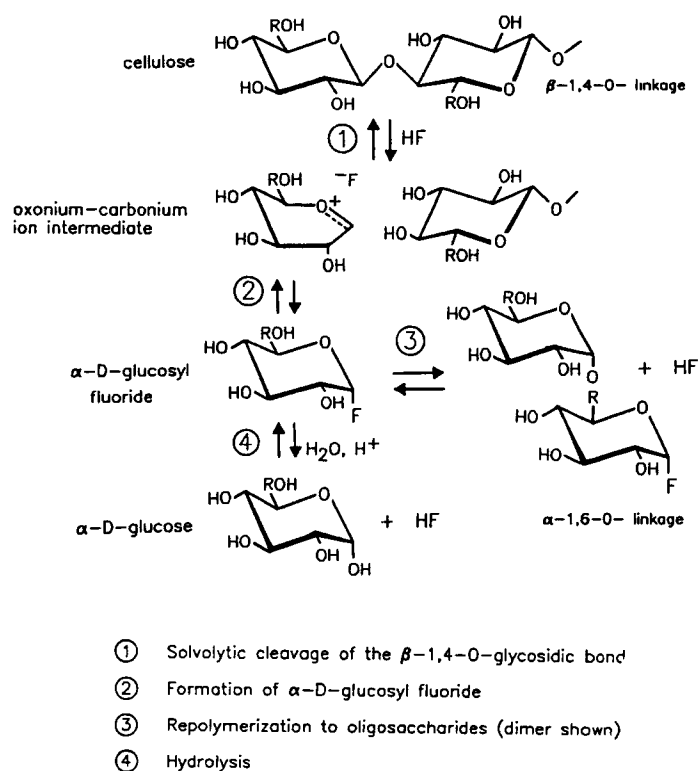|	
①	Solvolytic cleavage of the β–1,4–O–glycosidic bond
②	Formation of α–D–glucosyl fluoride
③	Repolymerization to oligosaccharides (dimer shown)
④	Hydrolysis

Fig. 7. Mechanism for the HF-solvolysis of cellulose and glucosyl fluoride repolymerization.

products rapidly dissolved away from HF-reacted solid and dispersed in solution. The water also hydrolyzed glucosyl fluoride to glucose. Although this product solution was weakly acidic owing to presence of dissolved HF, hydrolysis of the reversion oligosaccharides did not occur at room temperature. Further, in the experimental protocol, the product solution was immediately neutralized to pH 5–7 by addition of $CaCO_3$ powder, which precipitated the dissolved HF as CaF_2 solid.

The oligosaccharide product distribution in the *water soluble* reaction products *before* posthydrolysis was profiled by High-Performance Liquid Chromatography (HPLC). Specifically, free glucose and oligosaccharides of degree of polymerization (DP) of 2 to 6 were separated on a Bio-Rad HPX-42A HPLC-oligosaccharide analysis column (analysis conditions: 0.6 mL/min HPLC-grade H_2O mobile phase, 85°C column temperature, and differential refractive index (RI) detection) at range of 2×. Oligosaccharides of DP 6 to 10 were not well separated, and oligosaccharides of DP > 10 voided the column.
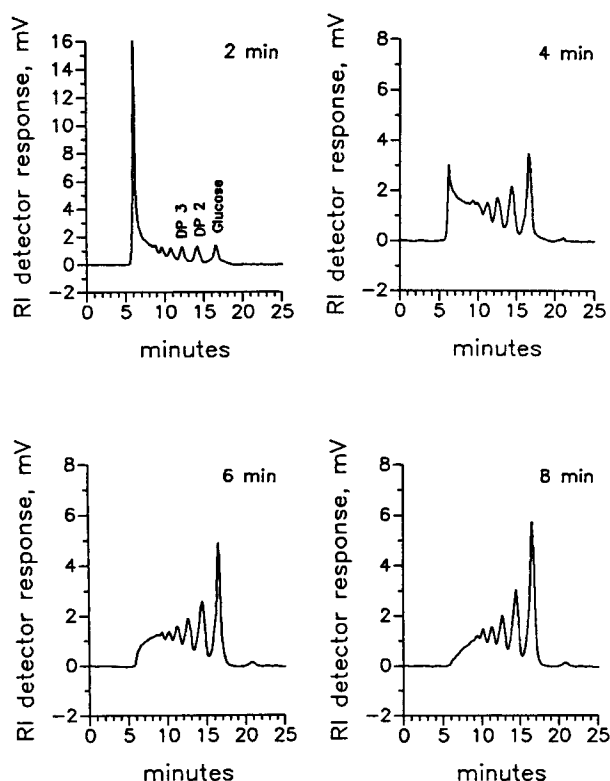
Fig. 8. Solvolysis of a single, dry prehydrolyzed wood chip by a 100% HF vapor stream at $T_g=31°C$: HPLC-oligosaccharide profiles before posthydrolysis as a function of reaction time. Column loading: 100 μg total oligomer.

Effect of Reaction Time

HPLC oligosaccharide profiles obtained from the solvolysis of *dry* prehydrolyzed wood by an anhydrous, 100% HF vapor stream at 31°C, and reaction times from 2 to 8 min are presented in Fig. 8. Although the cellulose fraction was completely converted to water-soluble products within a 2 min reaction time, the oligosaccharide product distribution continued to shift toward monomer as a function of reaction time from 2 to 8 min. At 8 min, the oligosaccharide product distribution settled to equilibrium. At a given temperature, an equilibrium oligosaccharide product distribution was obtained when the rate of formation of oligosaccharide by gluosyl fluoride repolymerization equaled the rate of solvolysis of oligosaccharides.

Effect of 100% HF Vapor Temperature

HPLC oligosaccharide profiles obtained from the solvelysis of *dry*, prehydrolyzed wood by an anhydrous, 100% HF vapor stream at 31°C
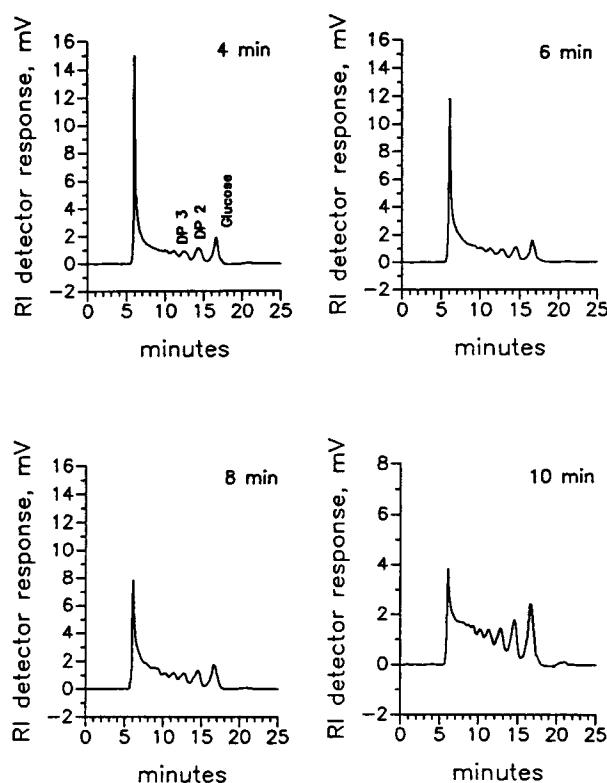
Fig. 9. Solvolysis of a single, dry, prehydrolyzed wood chip by a 100% HF vapor stream at $T_g = 41\,^\circ C$: HPLC-oligosaccharide profiles before posthydrolysis as a function of reaction time. Column loading: 100 μg total oligomer.

and 41 $^\circ C$ are compared in Figs. 8 and 9, respectively. Note that as the 100% HF vapor stream temperature increased, the extent of reversion (i.e., the average DP of the oligomers) increased dramatically.

At a 100% HF vapor stream temperature of 52 $^\circ C$, most of the oligosaccharides had a DP > 10, and so these higher oligomers were not retained by the Bio-Rad HPX-42A column. However, these oligomers were still completely soluble in water, probably owing to branching of the oligosaccharide structures, which inhibits crystallization.

As the temperature increases, the extent of glucosyl fluoride repolymerization increases. Since glucosyl fluoride repolymerization regenerates HF by condensation, HF desorption and recovery is facilitated at higher temperatures. However, the reaction products must be "post hydrolyzed" to recover glucose from the reversion oligosaccharides.

In all experiments, *dry* lignocellulose wafers were reacted with *anhydrous* HF vapor. If moisture was present in the substrate, then *in situ* hydrolysis of glucosyl fluoride to glucose, and regeneration of HF will

Table 2

Glucose Yields Before and After Posthydrolysis of Water-Soluble Reaction Products

Reaction Time	T_g	Glucose Yield Before Posthydrolysis		Glucose Yield After Posthydrolysis	
min	°C	g/g	χ^a	g/g	χ^a
2.0	31	0.066	7.9	0.745	89.8
4.0	31	0.216	26.0	0.786	94.7
6.0	31	0.211	25.4	0.773	93.1
8.0	31	0.253	30.5	0.793	95.5
2.0	41	0.033	4.0	0.620	74.7
4.0	41	0.080	9.6	0.749	90.2
6.0	41	0.073	8.8	0.764	92.0
8.0	41	0.118	14.2	0.766	92.3
10.0	41	0.090	10.8	0.807	97.2
6.0	52	0.040	4.8	0.793	95.5
8.0	52	0.034	4.1	0.776	93.4
10.0	52	0.053	6.4	0.775	93.3

[a] χ of maximum theoretical glucose yield.

occur (*see* Fig. 7). The hydrolysis would compete with the glucosyl fluoride available for repolymerization, and thus, shift the oligosaccharide product distribution toward monomer. However, the effect of lignocellulose moisture content on the oligosaccharide product distribution was beyond the scope of this study.

Glucose Yields Before and After Posthydrolysis

The water-soluble reaction products from the vapor-phase HF solvolysis of prehydrolyzed wood are a mixture of glucose and reversion oligosaccharides. A dilute-acid posthydrolysis of the water-soluble products at mild conditions (in the experimental protocol, 2 N TFA at 121°C for 1 h) readily converted the reversion oligosaccharides back to glucose without degradation. For the oligosaccharide profiles given in Figs. 8 and 9, the glucose yields both before and after posthydrolysis are compared in Table 2.

CONCLUSIONS

The solvolysis of a single prehydrolyzed wood (lignocellulose) wafer (1.0 cm/side, 0.4 mm thick) in an anhydrous, 100% HF vapor stream at 1.0 atm was studied by exploring the effect of 100% HF vapor temperature (30 to 80°C on (1) HF adsorption and desorption, (2) reaction rate and glucose yield, and (3) glucosyl fluoride repolymerization. In general, all three processes are coupled, and 100% HF vapor temperature is the key process variable that controls these processes.

The HF loading (g HF adsorbed/g lignocellulose) decreased with increasing HF vapor temperature ($\theta_e = 1.42$ HF/g lignocellulose at 31°C, 0.382 g HF/g lignocellulose at 60°C) consistent with a physical adsorption process. Adsorbed HF was the limiting reagent for lignocellulose solvolysis: 0.4 g HF/g lignocellulose was required for saturation of hydroxyl groups and solvolysis of the glycosidic linkages in the cellulose fraction.

The glucose yield vs time curve decreased with increasing temperature. As the temperature increased, the intrinsic rate constant for cellulose solvolysis increased, but the HF loading on the solid that the cellulose perceived for solvolysis decreased. Therefore, the Arrhenius kinetics of cellulose solvolysis and the thermodynamics of HF physical adsorption work in opposing directions with increasing temperature. This coupling determined the overall decrease of the glucose yield vs time curve with increasing HF vapor stream temperature.

The extent of glucosyl fluroide repolymerization, as measured by HPLC-oligosaccharide profiling, increased with increasing HF vapor temperature. Since glucosyl fluoride repolymerization generates HF by a condensation reaction, glucosyl fluoride reversion is coupled to HF desorption and recovery. Over the range of reaction conditions considered, glucosyl fluoride repolymerization was significant. However, after posthydrolysis of water-soluble reaction products, glucose recoveries averaged 94% of theoretical, provided the HF loading on the lignocellulose was greater than the minimum of 0.4 g HF/g lignocellulose.

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