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REACTION RATES FOR GAS-PHASE HYDROGEN
FLUORIDE SACCHARIFICATION OF WOOD

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REACTION RATES FOR GAS-PHASE HYDROGEN FLUORIDE SACCHARIFICATION OF WOOD

By

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ABSTRACT

REACTION RATES FOR GAS-PHASE HYDROGEN FLUORIDE SACCHARIFICATION OF WOOD

By

Gregory Lawrence Rorrer

The intrinsic reaction rates for gas-phase HF saccharification of cellulosic materials in Bigtooth Aspen were determined. Experimental techniques were developed to obtain sugar yield versus reaction time data from wood chips reacted with an HF/nitrogen gas-stream of fixed HF partial pressure and temperature. Mass-transfer effects were experimentally screened out by determining the regime where the reaction rate was independent of both flowrate and wood chip size.

The intrinsic glucose yield versus time data proceded by a sigmoidal profile. For pure HF flow at ambient reaction conditions (30 °C, 1.0 atm), the reaction achieved maximum glucose yields of 2.7 to 2.9 mmol/g-wood within 2 minutes. The glucose production rate decreased nonlinearly with decreasing HF partial pressure from 1.0 to 0.2 atm at 30 °C. Surprisingly, the glucose production rate decreased with increasing reaction temperature from 28 to 108 °C at an HF partial pressure of 1.0 atm, and this effect was not due to product degradation. Processes such as HF adsorption onto the lignocellulosic matrix may be coupled to cellulose solvolysis and may strongly influence the overall glucose production rate.

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INTRODUCTION

The conversion of lignocellulosic materials to simple sugars by acid hydrolysis is a well-established biomass saccharification technology. The acid hydrolysis of cellulosic materials in wood produces sugars that can be readily fermented to ethanol or other useful chemicals. However, the saccharification of wood by conventional sulfuric and hydrochloric acid hydrolysis processes suffers from a variety of drawbacks, including low sugar yields, high acid consumption, long reaction times, and high temperatures and pressures required to drive the cellulose hydrolysis (1).

The use of anhydrous hydrogen fluoride (HF) to "crack" cellulosic materials in wood overcomes the aforementioned process inefficacies plaguing other conventional acid hydrolysis technologies. The "HF saccharification" of lignocellulosic materials offers 1) high sugar yields, 2) no product degradation, 3) short reaction times, 3) ambient reaction conditions, 4) low acid consumption due to efficent recovery and recycle of HF, and 5) no elaborate substrate pretreatment except for drying. Actually, the process of "HF saccharification" is not a direct hydrolysis of the cellulose chain. The solvolysis of cellulose (a beta-1,4 linked polyglucan) proceeds by a glycosyl fluoride intermediate, which is readily hydrolyzed in even a stoichiometric amount of water to yield glucose and regenerate HF (2). The solvolysis of xylan in wood procedes similarly.

The first serious studies of the "HF saccharification" of wood were initiated by several German investigators in the early 1930's. Apparently, gas-phase HF saccharification of wood reached the pilot-plant stage just prior to World War II. Most notably, Hoch and Bohunek (1937) developed a process to react wood chips with gaseous HF at a reduced pressure of 30 mm Hg and temperature of 35 to 40 °C (3). After about 30 minutes, the reaction was complete. The reaction was followed by excess HF desorption at 62 °C. Luers (1938) summarzied the results of a I.G. Farben pilot plant study which utilized the Hoch and Bohunek process (4). Gas-phase HF saccharification of wood was studied as a function of reaction time to maximum yield, temperature, HF concentration, and HF amount. Batch reactions that were carried out with 40 kg of pure HF per 100 kg of wood at 2 to 3% moisture gave the best results: 50% and 57% of reducing sugars were obtained from pine and beechwood respectively. Optimal reaction times and temperatures were not specified, and many of the original results were lost.

The advent of World War II drew attention away from "HF saccharification", and after World War II, the technology was essentially "forgotten". Research in "HF saccharification" was renewed following several "energy crises" in the mid 1970's by several investigators interested in novel biomass conversion technologies. Early, it was evident that the advantages of "HF saccharification" lay in the unique chemical reaction engineering and chemical kinetic aspects of the process. In this light, Selke _et al_. studied the reaction kinetics of liquid-phase HF saccharification of wood (Bigtooth Aspen) and pure cellulose in a well-stirred batch-reactor (5,6). Total, water-soluble glucose and xylose yield data were obtained as a function of reaction time (0 to 60 min), temperature (-12 to 4°C), and water content in HF (0 to 6.4% by weight). For example, at 0°C, anhydrous, liquid HF readily "cracked" cellulosic materials to produce glucose and xylose yields in excess of 90% of maximum theoretical, typically within 20 to 30 minutes. The reaction rate was independent of particle size for wood chips of 0.05 to 0.2 cm thickness. The reaction kinetics were reasonably described by a homogeneous, psuedo-first order rate model (6). Also, preliminary process-design, economic, and technology assessment studies by Hawley _et al_. indicated that although HF saccharification lacks sufficient process technology development, it may possess basic advantages over the more-developed acid-hyrolysis technologies (1,7).

Recently (1982), pilot-plant studies for the gas-phase HF saccharification of poplar were intiated by Ostrovski _et al_. at Canertech of Canada in the attempt to commercialize this process (8). The process used a semi-continuous test reactor of 20 kg wood (per charge) capacity that featured an

HF adsorption/reaction stage, followed by an HF-desorption stage at elevated temperature. Reaction products underwent dilute-sulfuric acid post-hydrolysis at 140°C to yield free sugars and re-convert reversion oligosaccharides to monomeric sugars (glucose and xylose). Pentosans and hexosans were then fermented to yield a supposed 438 liters of ethanol per tonne of dry wood. Results of their initial pilot-plant studies demonstrate the feasiblility of gas-phase HF saccharification of wood. They report that maximum glucose yields of 90% and xylose yields of 70% were typically obtained, with 99% of total HF recycled. The optimum conditions for HF saccharification of poplar occurred under a 100% HF flow at ambient temperature and pressure (9).

Apparently, gas-phase HF saccharification of wood possesses several advantages over the liquid-phase process. Gas-phase HF saccharification of wood offers rapid reaction rates and greater flexibility of reactor operating conditions. Gas-phase HF solvolysis of cellulosic materials in wood can be carried out at higher temperatures (the liquid phase is limited to 19.8°C, the normal boiling point of HF), and pressures. The anhydrous HF concentration can be easily diluted in inert gas. The recovery of HF is simpler and more efficient because excess HF does not have to evaporated off the solid. The HF to wood requirements are also lower, owing to the reduced density of HF in the gas-phase.

Gas-phase HF saccharification of wood can be more quantitatively assessed by developing reactor models that predict the rate of cellulose cracking and sugar product yield as a function of reactor operating conditions. However, such models require an intrinsic chemical kinetic model which predicts the rate of cellulose cracking and sugar yield as a function of reaction time, reaction temperature and gas-phase HF concentration (or HF partial pressure). Unfortunately, no chemical kinetic studies of gas-phase HF saccharification of wood have been reported in the literature. Therefore, a fundamental chemical reaction engineering study is needed to elucidate and model the heterogeneous rate processes which characterize the solvolysis of cellulosic materials in wood by gaseous, anhydrous HF. The purpose of this investigation is to generate intrinsic reaction-rate data for the gas-phase HF saccharification of wood so that the intrinsic rate processes and chemical kinetics that characterize this process can be elucidated.

EXPERIMENTAL

Reaction rates for the solvolysis of cellulosic materials in wood by gaseous HF were determined from total, water-soluble glucose and xylose yield versus reaction time data acquired at a fixed set of reaction conditions. Rate data were obtained from Bigtooth Aspen chips reacted with an HF/nitrogen gas-stream of fixed HF partial pressure and temperature.

Reaction Apparatus

The batch-mode reaction between a single wood chip and an anhydrous HF/nitrogen gas-stream is contained in the reaction apparatus shown in Figure 1. The reaction apparatus is designed to 1) set and monitor the gas-stream reaction conditions, 2) carry out the reaction and still allow easy access of the wood-chip sample, and 3) neutralize the effluent HF gas-stream. All HF-wetted parts are constructed of monel, teflon, or similar HF-resistent materials. The reaction apparatus is contained in a fume hood.

HF is supplied in liquid form from Matheson Gas Products. A heating jacket surrounding the HF tank keeps the surface of the HF tank at 50 C (safety limit) and thus

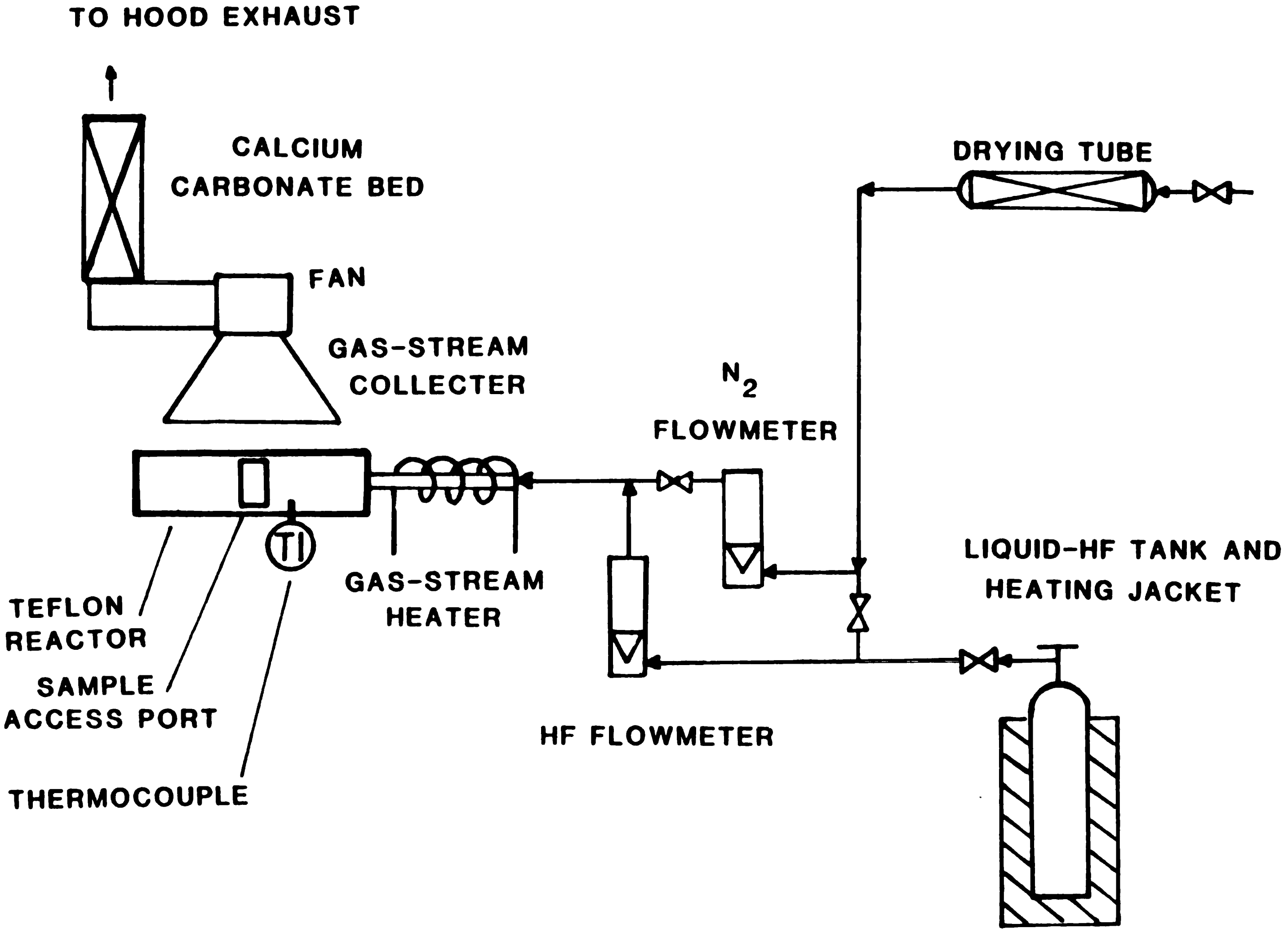

FIGURE 1. Reaction Apparatus.

provides the heat and driving force for HF vaporization and flow (the normal boiling point of HF is 19.8°C). HF and nitrogen are metered separately by stainless steel and glass-bore float flowmeters respectively. The HF flow is in high stoichiometric excess relative to the cellulosic materials in the wood chip available for reaction. Therefore, the HF concentration in the feed-stream is the HF concentration in the reactor. The HF and nitrogen are mixed and heated by an electrical resistance heater that sets and isothermally maintains the gas-stream to +/- 0.5 °C. The gas-stream is then fed into the reactor.

In the reactor, the wood chip wafer is held perpendicular to the gas-stream by a teflon sample holder inserted into the sample access port. Total pressure in the reactor is 1.0 atm. The HF partial pressure in the reactor is determined from the HF and nitrogen molar flowrates and the total pressure. The gas-stream exits the reactor at the sample access port and is drawn upward into an induction fan, which then blows the gas stream into a packed bed of calcium carbonate. Here, HF in the gas-stream is neutralized to calcium fluoride. Any HF that is not neutralized is vented into the exhaust.

Procedure

Wood wafers of ca. 400 micron thickness are microtomed from roughly chipped Bigtooth Aspen (Michx), cut into square tablets of ca. 0.75 cm on-a-side, dried "in vacuo" over phosphorous pentoxide and weighed (typical weight is 20 mg). The HF/nitrogen flowrates and gas-stream temperature are set and allowed to stabilize. A single wood chip sample is contacted with the HF/nitrogen gas-stream in the reactor for a given reaction time. If necessary, the wood chip sample is pre-heated to the desired reaction temperature prior to reaction. In the reactor, the cellulosic and hemicellulosic materials in the wood chip are "cracked" primarily to glycosyl and xylosyl fluorides, which reside as solids on the lignocellulosic matrix.

After a specified reaction time, the HF-reacted wood chip sample is removed from the reactor. Immediately thereafter, the reaction is quenched in ca. 2 ml distilled water containing a known inclusion of myo-inositol, an internal standard used for later quantitative chromatography of the sugar product. During the quenching process, sugar fluorides residing on the lignocellulosic matrix dissolve and hydrolyze to yield free sugars (D-glucose, D-xylose, and minor amounts of other sugars) and regenerate the reacted HF. Various reversion reactions between free sugars and sugar fluorides that occur during the quenching process produce a distribution of alpha-1,6 linked water-soluble oligosaccharides of 1 to 6 sugar units in size (10).

The sugar product solution is neutralized by precipitating the HF out of solution. Calcium carbonate powder is added to the quenched reaction mixture, which precipitates HF to calcium fluoride. The neutralized sugar solution is centrifuged from the insoluble fraction of the reaction mixture (unreacted cellulose, lignin, calcium fluoride, and calcium carbonate), decanted, and frozen for storage.

The reaction procedure is repeated for a new wood chip sample at a new set of reaction conditions. Each wood chip sample is reacted for a given reaction time at constant gas-stream temperature and HF partial pressure. The reaction time, temperature, HF and nitrogen flowrates are recorded for each sample reaction. The complete range of reaction conditions for this experimental program are summarized in Table 1. The key experimental assumptions used to analyze the reaction-rate data are summarized in Table 2.

Sugar Analysis

Reversion oligomers are converted back to momomeric sugars (D-glucose and D-xylose primarily) by dilute acid post-hyrolysis. Prior to sugar analysis, and assay volume (50 µl typically) is hyrolyzed in 200 µl of 2 N trifluoroacetic acid (TFA) at 121°C for 1 hr. These post-hydrolysis conditions are optimized to recover the maximum total monomer sugar yield with negligible glucose product degradation to 5-(hyroxymethyl)-2-furfuraldehyde (5-HMF) (10).

Following post-hydrolysis, the sugars are separated, identified, and quantified directly by High-Performance

Table 1. Summary of reaction conditions.

SUBSTRATE: Bigtooth Aspen (Populus grandidentata) wood chip wafer

WOOD CHIP SIZE: 0.4 mm thick, 0.75 cm/side, 20 mg microtomed with grain of wood

HF FLOWRATE: 3.8 to 13.4 mmol/sq cm-min

NITROGEN FLOWRATE: 0 to 44 mmol/sq cm-min

TOTAL PRESSURE: 1.0 atm

HF PARTIAL PRESSURE: 0 to 1.0 atm

TEMPERATURE: 28 to 108°C

REACTION TIME: 0 to 15 min

Table 2. Assumptions.

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1. No heat or mass-transfer effects.
2. Isothermal reaction conditions.
3. HF in high stoichiometric excess relative to wood chip.
4. Constant HF partial pressure.
5. Anhydrous reaction conditions.
6. Intact lignocellulosic matrix.
7. All reaction products reside on the lignocellulosic matrix.
8. Cellulose solvolysis is irreversible and chain-length independent.
9. Quench of reaction in water is instantaneous and complete.
10. Glucose yield has 1:1 molar correspondence to glycosyl fluoride product.
11. Theoretical maximum glucose yield of 3.441 mmol/g-wood for Bigtooth Aspen (6).
12. Theoretical maximum xylose yield of 1.4 mmol/g-wood for Bigtooth Aspen (6).

Liquid Chromatograhy (HPLC), or indirectly by Gas-Liquid Chromatography (GLC) via alditol-acetate derivatization (11). The yield of each monomeric sugar obtained from the HF-reacted wood chip is back-calculated by the "internal standard" method. The yield of each sugar is normalized to a basis of millimole of sugar obtained per gram of original unreacted wood.

RESULTS AND INTERPRETATION

Intrinsic glucose and xylose yield versus reaction time data were obtained from Bigtooth Aspen reacted with an HF gas-stream of specified HF partial pressure and temperature. To insure acquisition of intrinsic reaction rate data, the mass transfer resistances to the reaction rate were experimentally screened out. The effect of HF partial pressure at constant gas-stream temperature on the time-dependent evolution of glucose and xylose yield was examined. Similarly, the effect of reaction temperature at constant HF partial pressure on the time-dependent evolution of glucose and xylose yield was also explored. The results and interpretation of this experimental program will now be detailed.

Elimination of Mass Transfer Resistances

The global (experimentally observed) reaction rate evaluated at the bulk gas HF concentration is the intrinsic reaction rate provided the effective wood chip size is sufficiently small to eliminate intra-particle mass-transfer resistances, and the superfacial mass velocity over the wood chip is sufficiently large to eliminate convective (external) mass-transfer resistances. Normally, mass-transfer resistances are manifested as HF concentration gradients near and within the wood chip, and would thus lower the overall reaction rate. Experimentally, mass-transfer resistances to the rate of cellulose solvolysis by HF vapor were assumed eliminated when the glucose yield after a specified reaction time was independent of both pure HF flowrate and wood chip thickness.

For pure HF at 30°C flowing over a wood chip of 0.4 mm thickness, the glucose yield obtained after a 60 second reaction time was independent of HF superfacial mass-velocities greater than 0.076 g/sq. cm-min. The superfacial mass-velocity is calculated from the molar flowrate assuming the gas-stream has a molecular weight of 20. This independence was verified by the null-hypothesis test. Glucose yield versus HF flowrate data are presented in Figure 2. Later, it was found that the maximum reaction rate for gas-phase HF solvolysis of of cellulose in wood occurred under these reaction conditions. Therefore, the reaction is controlled by intrinsic rate processes for any HF partial pressure from 0 to 1.0 atm and gas-stream temperature from 28 to 108°C. Note from Figure 2 that for HF flowrates from 0 to 0.076 g/sq. cm-min, the rate of cellulose solvolysis is shifting regimes, possibly from external mass-transfer control to intrinsic-rate control. However, a detailed discussion of mass-transfer effects is beyond the scope of this investigation.

Internal mass-transfer resistances were assumed

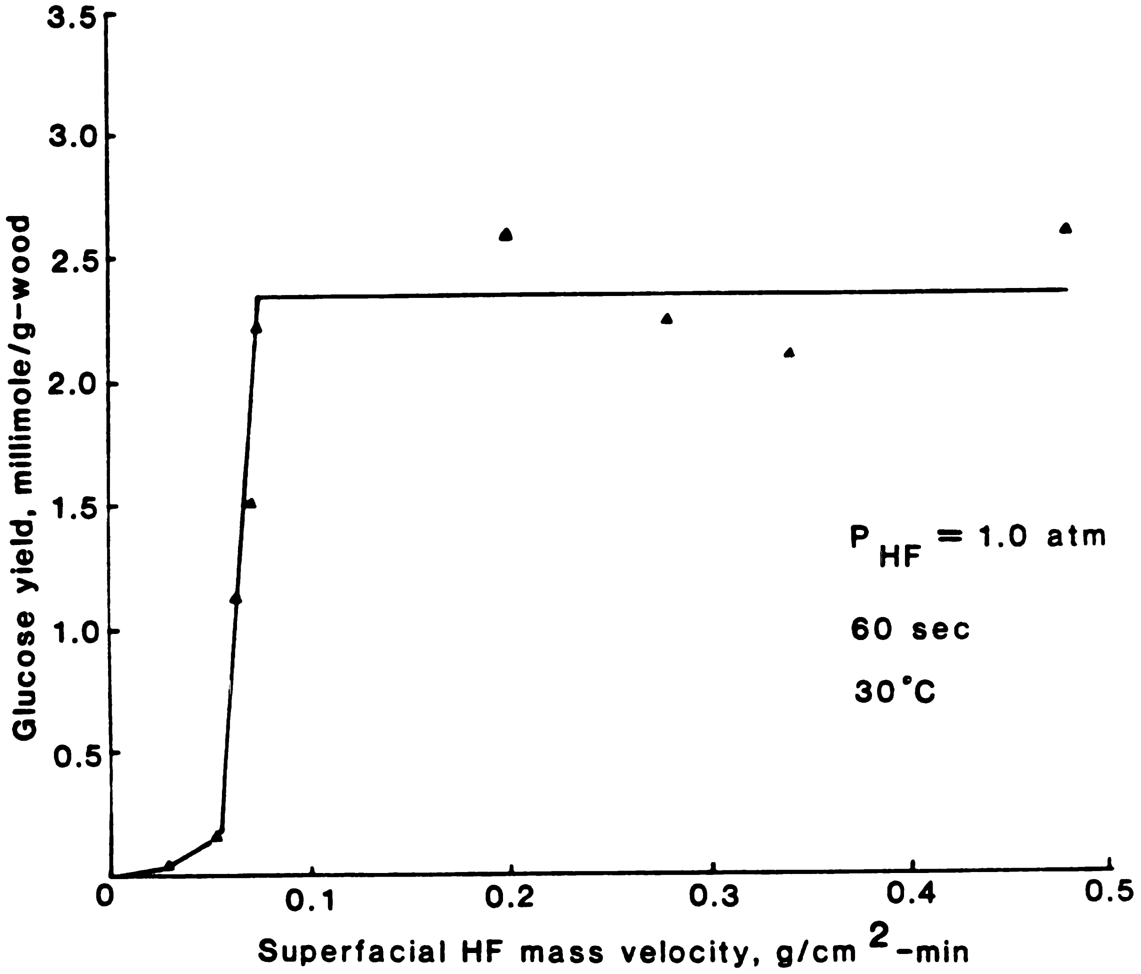

FIGURE 2. Glucose yield versus HF flowrate.

negligible for a wood chip wafer thickness of 0.4 mm. This assumption is based on previous studies of the effect of particle size on reaction rate for liquid-phase HF saccharification of wood (6), the high porosity of Bigtooth Aspen (ca. 55%) (5), and the high diffusivity of the small HF (1 angstrom) molecule. Likewise, it was assumed that when mass-transfer resistances were eliminated, heat transfer resistances were eliminated as well, and so no temperature gradients existed near and within the wood chip. This assumption is supported by the low heat of reaction for cellulose solvolysis by HF (ca. 6000 cal/g-mole) (5).

Glucose and Xylose Yield vs. Time Profile

Solvolysis of cellulosic materials in wood by gas-phase HF proceeded rapidly and consistently produced high glucose yields. Glycosyl fluoride reaction products were readily hyrolyzed to D-glucose with no apparent degradation.

In general, the glucose yield versus reaction time data possessed a sigmoidal profile at constant temperature and HF partial pressure. For example, at a pure HF flow greater than 76 mg/sq. cm-min at 30°C and 1.0 atm, the glucose yield versus time profile was sigmoidal and then leveled off to a maximum glucose yield of 2.7 to 2.9 millimole per gram of the original unreacted wood (80% to 85% of the theoretical maximum) within a reaction time of two minutes! These data are presented in Figure 3. The maximum theoretical yield

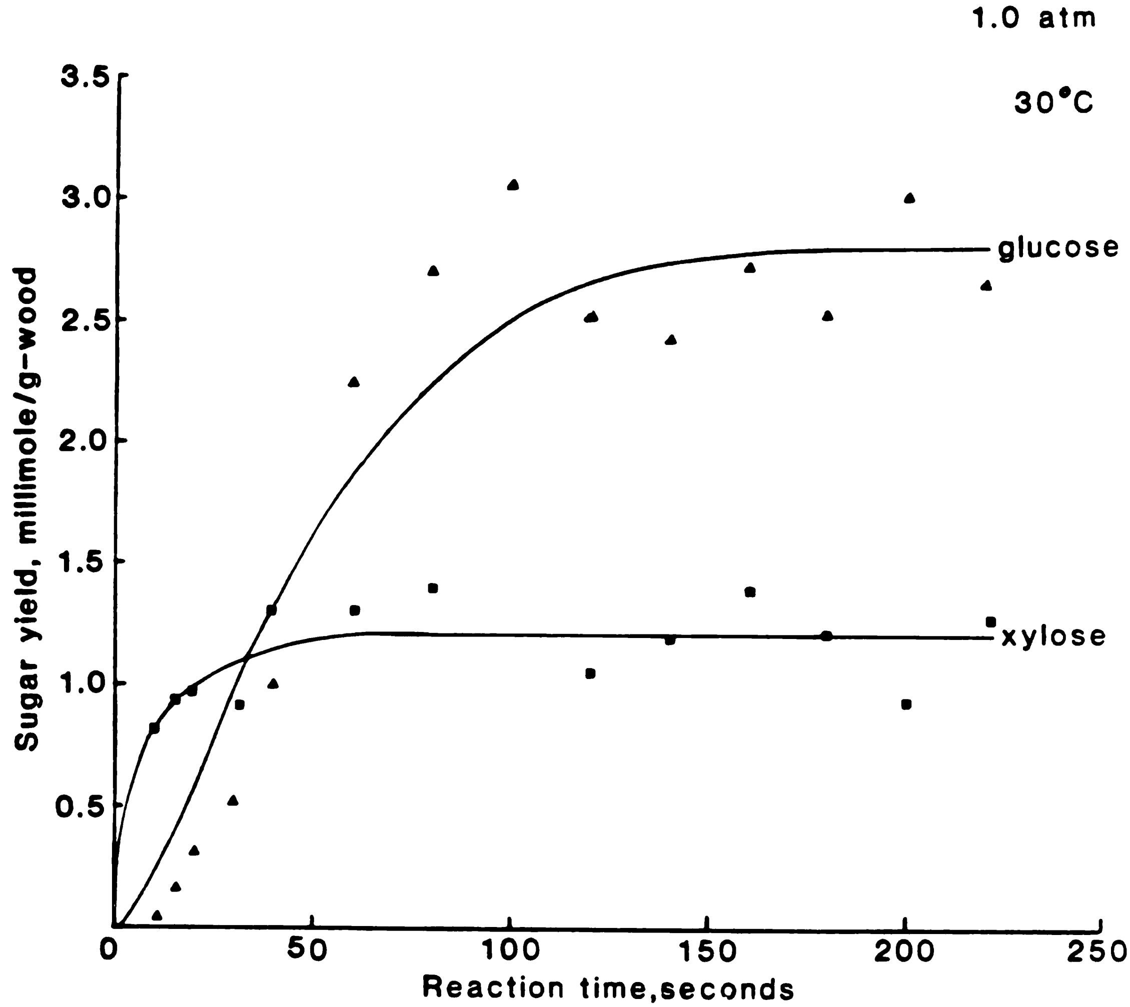

FIGURE 3. Glucose and xylose yield versus time profiles at 30°C.

for Bigtooth Aspen is 3.441 millimole per gram of wood (6). This value is approximate and based on previous material balance studies for liquid-phase HF saccharification of wood. The contribution of glucose from hemicellulose solvolysis was assumed negligible. No reaction product degradation was observed to occur for glucose yield-plateau data. If such degradation were to occur, then the glucose yield would pass through a maximum in time, as is the case with dilute-acid cellulose hydrolysis at elevated temperatures (12). Reaction products resided on the lignocellulosic matrix, and so there were no product losses to the gas-stream. Occasionally, glucose yields in excess of 90% were obtained, consistent with results of other investigators at Canertech. Based on all of the information provided above, this slight discrepancy in glucose yield cannot be explained. The scatter in glucose yield probably arises from inconsistencies in initial wood chip sample composition, errors in reaction time during the quenching process, (particularly at short reaction times), and errors in chromatographic sugar analysis.

Normally, the acid-catalyzed hydrolysis of cellulose is a random, stepwize depolymerization characterized by a monotone-decreasing time-dependent evolution of glucose. The solvolysis of cellulose in wood by gaseous HF is still considered a random, stepwize depolymerization. However, the sigmoidal profile of the intrinsic glucose yield versus time data suggests that other heterogeneous rate processes are coupled to the cellulose solvolysis. Candidates for these processes will be described later. Assume for now that the intrinsic reaction rate is determined by two sequential rate processes described by two independent, first-order rate equations governed by the intial condition of t=0, Y=0. The general solution of this system of rate equations can be used to fit glucose yield versus time data. It is given by

$$Y = a + be^{-ct} - de^{-ft} \qquad (1)$$

where a,b,c,d and f are adjustable parameters, t is the reaction time, and Y is the normalized glucose yield. The glucose production rate is determined from the time-derivative of equation (1), given by

$$\frac{dY}{dt} = dfe^{-ft} - bce^{-ct} \qquad (2)$$

Glucose yield versus reaction time data were curve-fitted to equation (1) by least-squares multiple nonlinear regression (13). For example, note from Figure 3 that the curve-fitting model described by equation (1) adequately predicted the sigmoidal profile and asymptotic leveling of the glucose yield versus time data. Because a complete rate model for gas-phase HF solvolysis of cellulose in wood has not yet been proposed, kinetic parameter estimation (i.e., rate constants, reaction orders, etc.) was not attempted.

In general, curve-fitted lines were not extrapolated beyond the upper reaction time limit of the data.

Gas-phase HF solvolysis of xylan in the hemicellulosic fraction of wood proceeded more rapidly than cellulose solvolysis at the same reaction conditions. For comparison, glucose and xylose yield versus time data are plotted together in Figure 3. Maximum experimentally attainable xylose yields of 0.9 to 1.2 millimole per gram of dry wood (65% to 85% of maximum theoretical) were achieved after approximately 1 minute. The maximum theoretical xylose yield in Bigtooth Aspen is 1.4 millimole per gram of dry wood, based on previous material balance studies for liquid-phase HF saccharification (6). The xylose product may have degraded to 2-furfuraldehyde during dilute-acid post-hydrolysis (10). However, the analytical procedures were not set up to detect for 2-furfuraldehyde. Inconsistency of xylose product degradation during post-hydrolysis, and possibly the non-uniformity of the initial xylan present in the wood chip sample created the scatter in the xylose yield. Additionally, the reaction time for high cellulose conversion was more than sufficient for high xylan conversion, and so kinetic data for xylan solvolysis was incomplete at low xylose yields. Therefore, curve-fitting of xylose yield versus reaction time data was not attempted. In any event, rate data acquisition focused on glucose yield because it is the more abundant and desired end-product.

Dependence of Reaction Rate on HF Partial Pressure

Glucose yield versus time data at 30°C for HF partial pressures from 0 to 1.0 atm (under 1 atm total pressure) are presented in Figures 4 and 5. Glucose production rate versus normalized glusose yield profiles at 30°C for each HF partial pressure are presented in Figures 6 and 7. Finally, glucose production rate versus reaction time profiles at 30 C for each HF partial pressure are presented in Figures 8 and 9.

In general, the intrinsic glucose yield versus time data possessed a sigmoidal profile at all HF partial pressures from 0 to 1.0 atm. The experimental maximum glucose yield of 2.7 to 2.9 millimole per gram of wood was independent of HF partial pressure. Even though long-time , yield-plateau data were not obtained for low HF partial pressures, the glucose yield did appear to converge on the experimental maximum, and not some lowered equilbrium value, as would be expected for a reversible reaction.

The glucose production rate at all reaction times uniformly and nonlinearly decreased with decreasing HF partial pressure. The glucose production rate consistently passed through a maximum between 10% and 20% of normalized glucose yield. Existence of a reaction rate maximum suggests that other intrinsic rate processes may be coupled to the cellulose solvolysis reaction.

Does the use of nitrogen as a diluent for HF

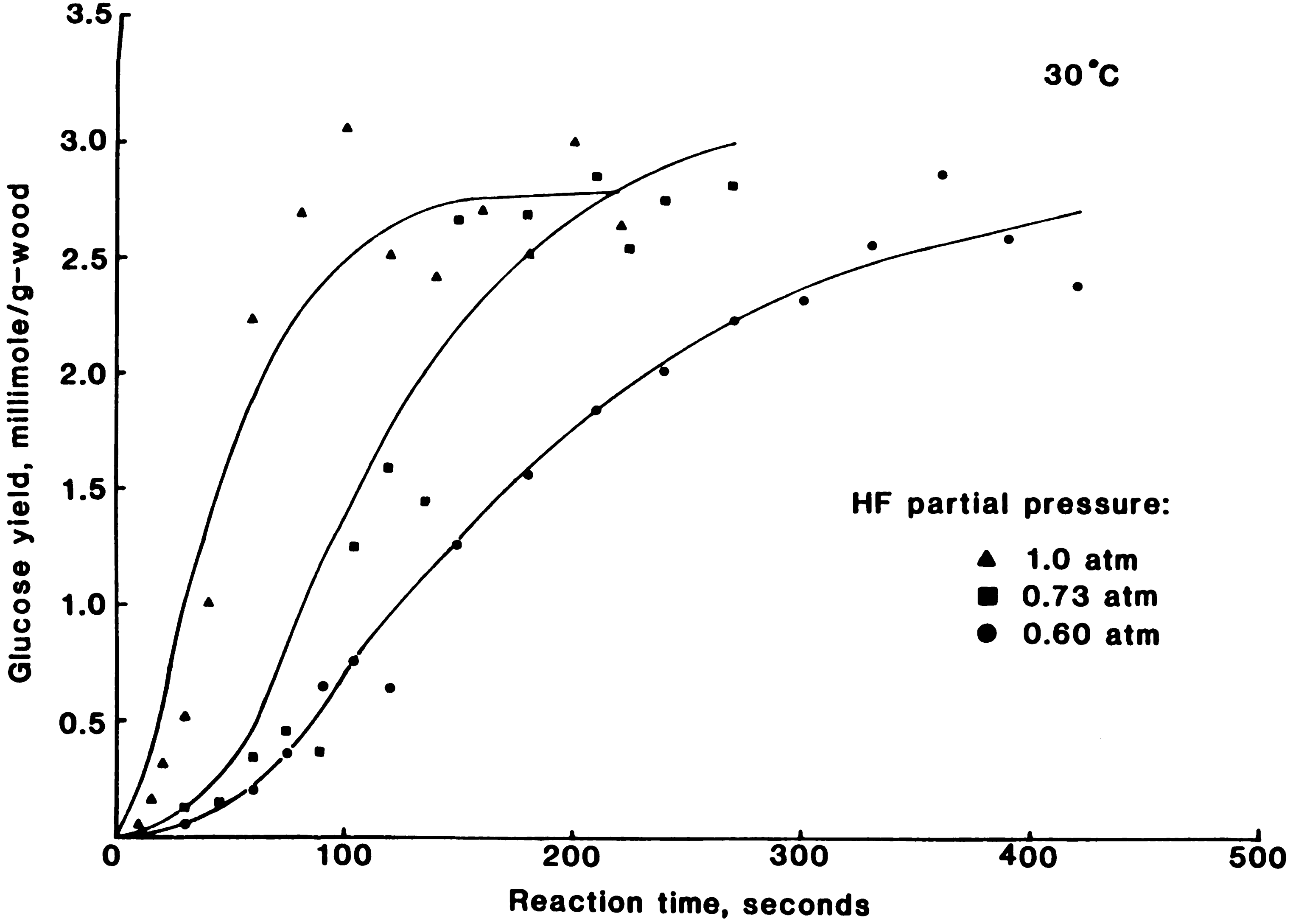

FIGURE 4. Glucose yield as a function of time for HF partial pressures from 0.6 to 1.0 atm at 30°C.

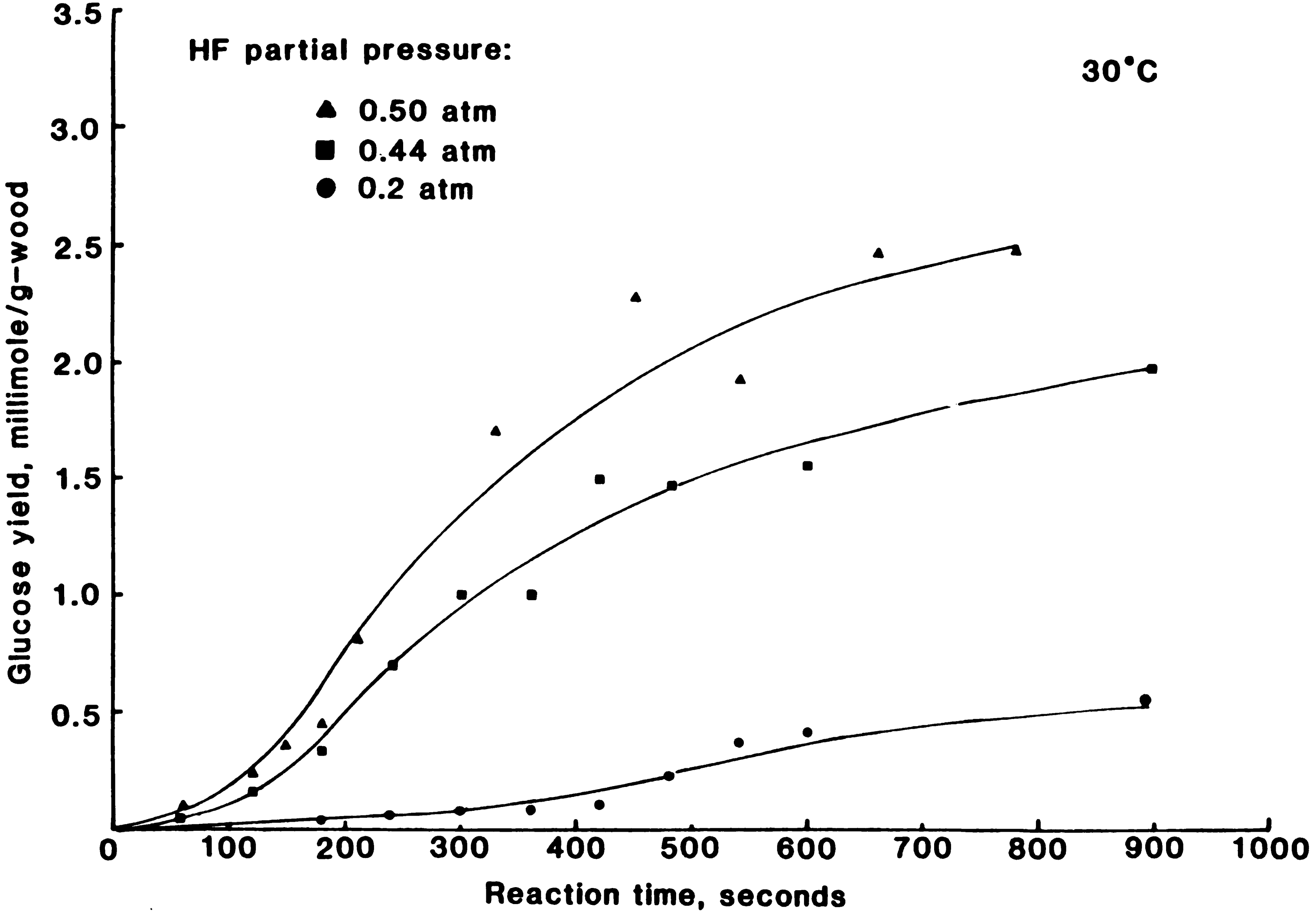

FIGURE 5. Glucose yield as a function of time for HF partial pressures from 0.2 to 0.6 atm at 30°C.

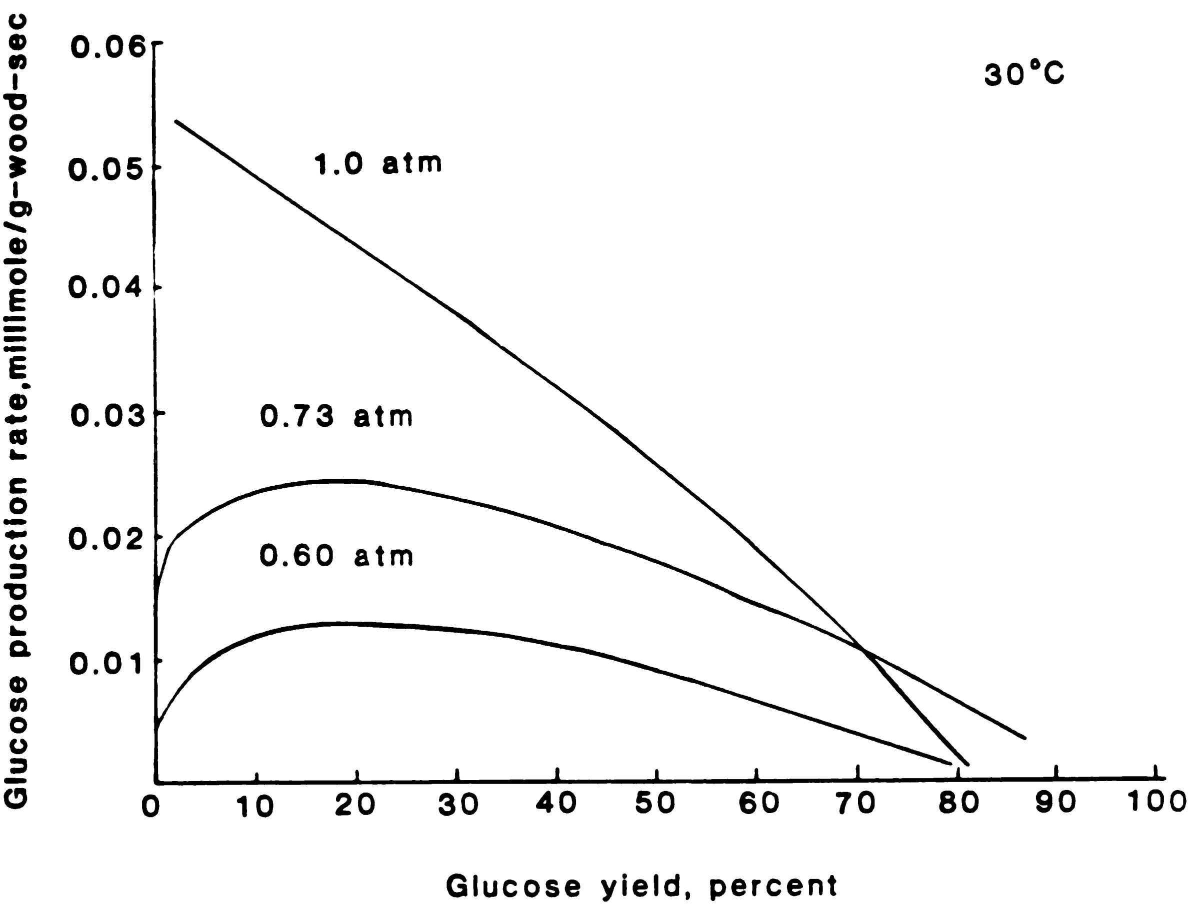

FIGURE 6. Glucose production rate versus glucose yield as a function of HF partial pressure from 0.60 to 1.0 atm at 30°C.

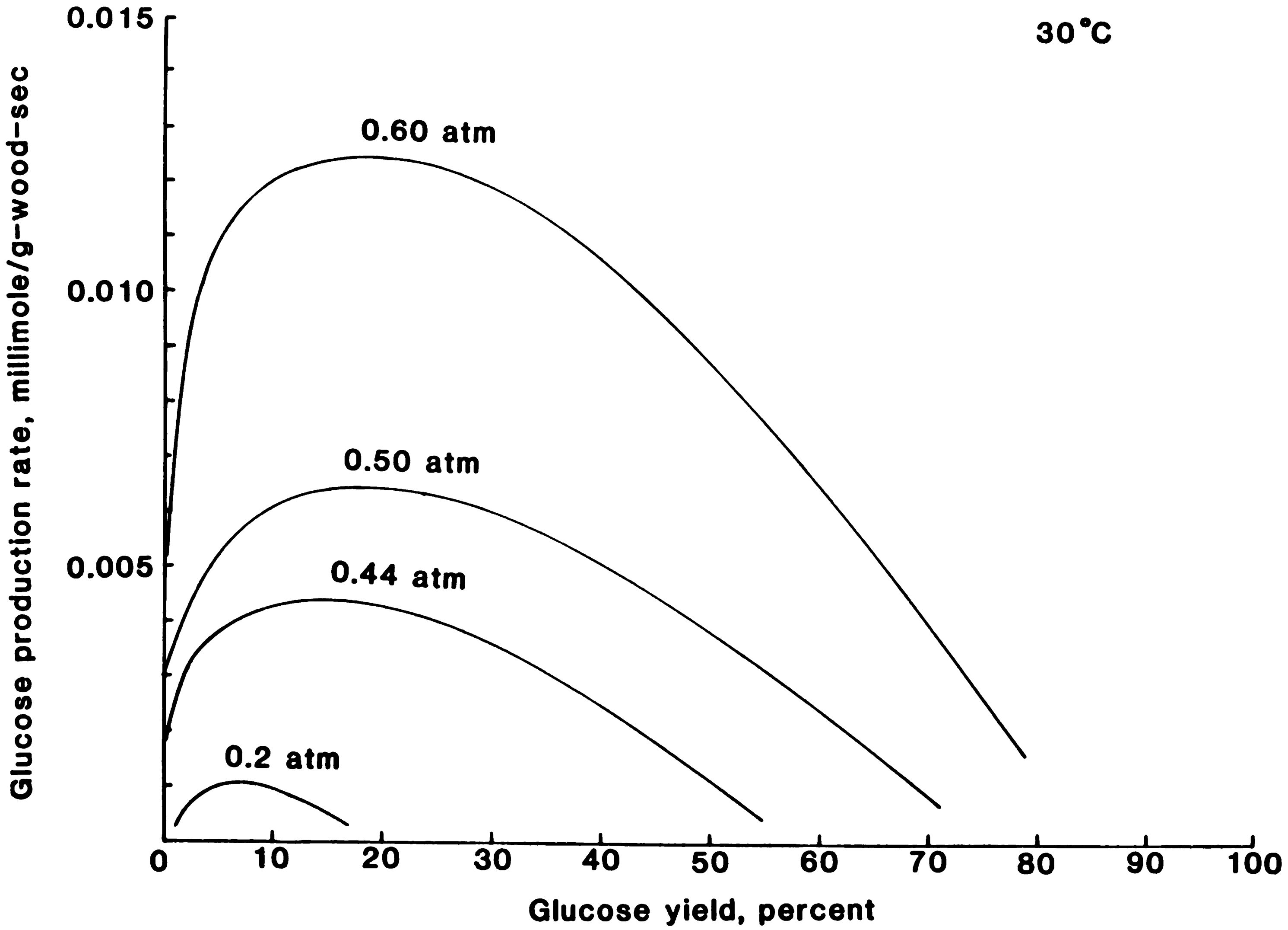

FIGURE 7. Glucose production rate versus glucose yield as a function of HF partial pressure from 0.2 to 0.6 atm at 30°C.

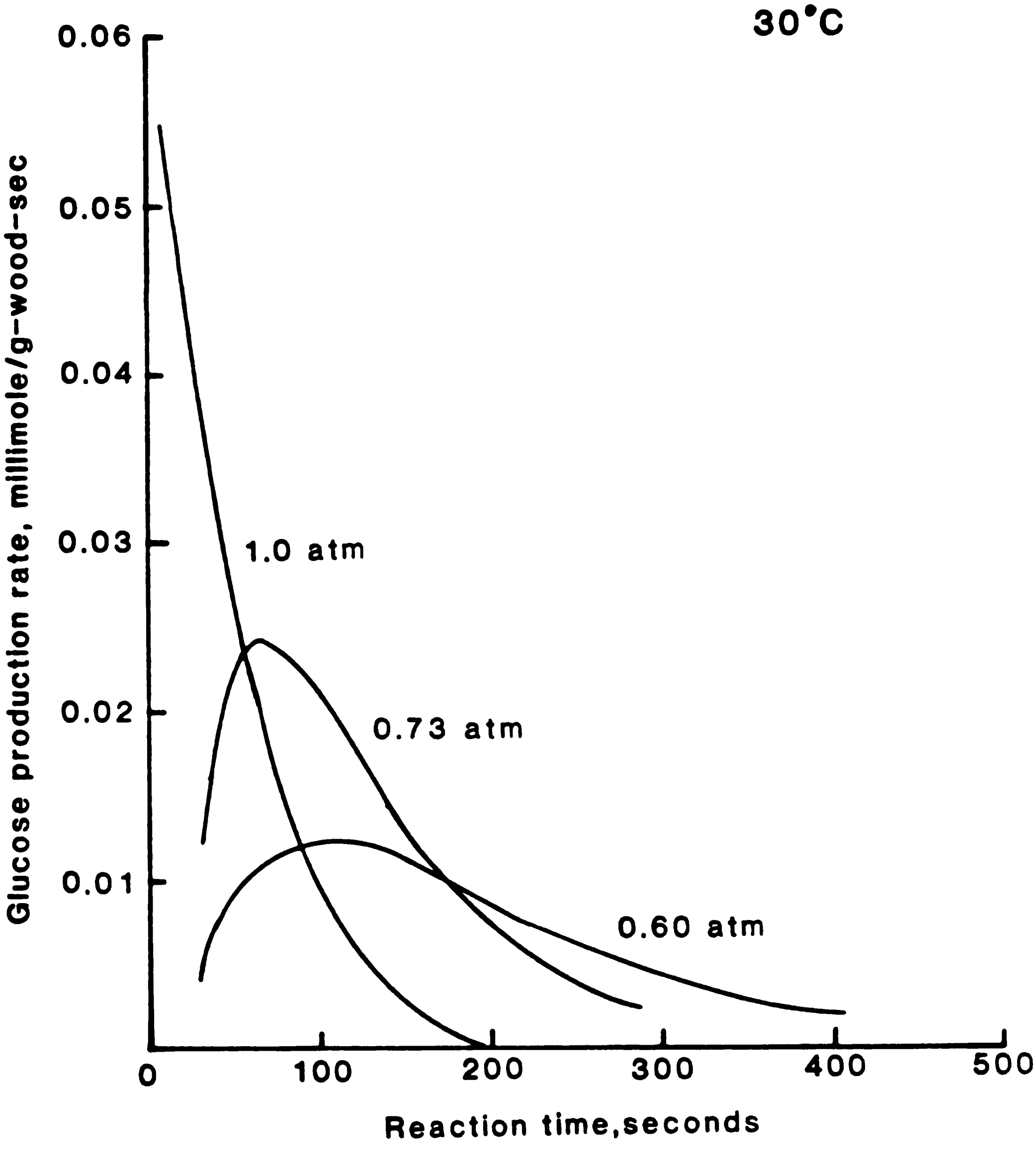

FIGURE 8. Glucose production rate as a function as time for HF partial pressures from 0.60 to 1.0 atm at 30°C.

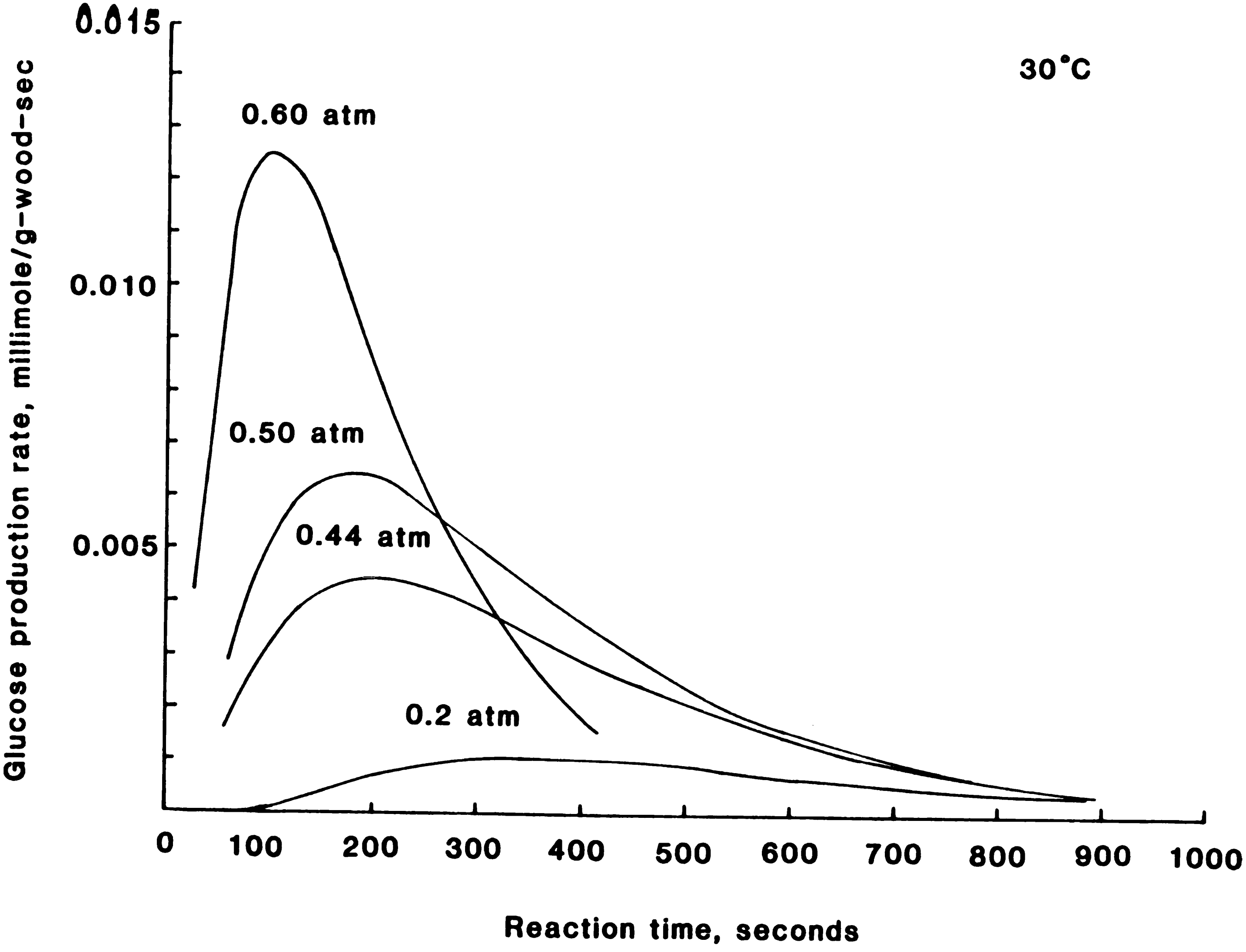

FIGURE 9. Glucose production rate as a function of time for HF partial pressures from 0.2 to 0.60 atm at 30°C.

concentration specifically effect the reaction rate? HF normally exists as a hydrogen-bonded hexomer in the pure vapor state at ambient conditions (14). The heat of mixing of HF in nitrogen was observed to be endothermic, with the corresponding drop in temperature of the mixed gas-stream proportional to the decrease in HF to nitrogen ratio. This phenomenon is attributed to disruption of hydrogen-bonded HF in the gas-phase. The feed-stream heater on the reaction apparatus compensated for the temperature drop and isothermally maintained the gas-stream at 30 °C. If the hexomeric form of HF is preferentially adsorbed on the surface of the lignocellulosic matrix (by virtue of its larger size), then the reaction rate would have a more pronounced dependence on an HF concentration that is set by dilution of pure HF in nitrogen as opposed to an HF concentration that is set by varying the total system pressure. However, the specific effect of "HF-depolymerization" could not be quantified experimentally with the apparatus and methods used.

Xylose yield versus time data for three representative HF partial pressures are presented in Figure 10. In general, xylose yield versus time data is broken up into two regimes. At short reaction times, a fraction of the hemicellulose is rapidly converted to xylose, followed by a much slower conversion of the remaining hemicellulose. Note that when the HF partial pressure was decreased, the initial fraction of hemicellulose converted to xylose also decreased. In general, decreasing the HF partial pressure

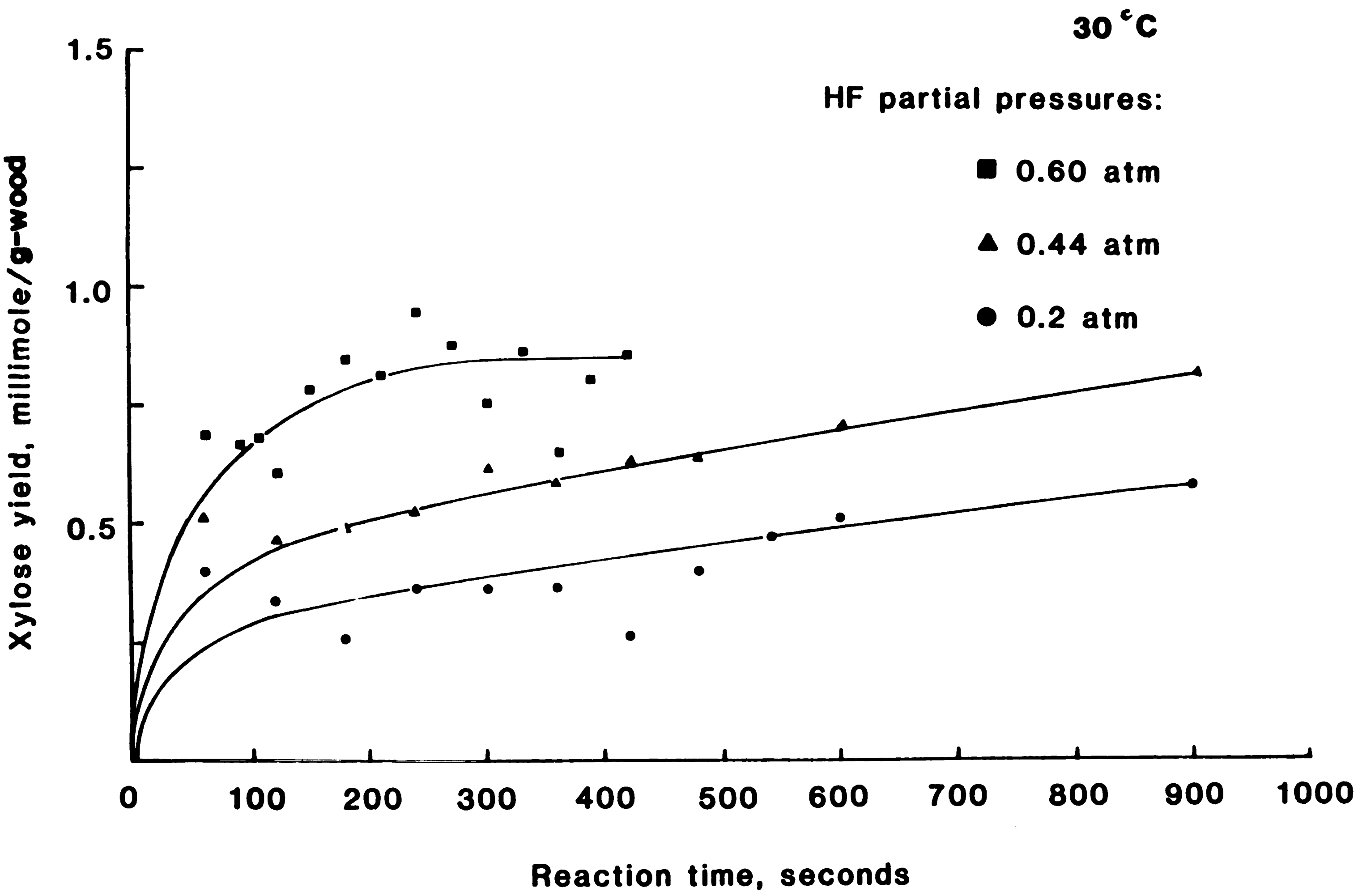

FIGURE 10. Xylose yield as a function of time for HF partial pressures from 0.2 to 0.60 atm at 30°C.

decreased the overall rate of xylose formation.

Dependence of Reaction Rate on Temperature

Isothermal glucose yield versus reaction time data obtained at an HF partial pressure of 1.0 atm for reaction temperatures from 28 to 108 C are presented in Figure 11. Isothermal glucose production rate versus normalized glucose yield profiles at each reaction temperature are presented in Figure 12. Isothermal glucose production rate versus reaction profiles at each reaction temperature are presented in Figure 13. Isothermal conditions for the complete reaction system (HF vapor and wood chip) were insured by pre-heating the wood chip to the desired reaction temperature in an oven prior to reaction. Sub-ambient, pure-HF gas-stream temperatures could not be attained at an HF partial pressure of 1.0 atm, because the normal boiling point of HF is 19.8°C. The HF gas-stream had to be at least 26 °C to provide a driving force for HF vaporization and flow.

The glucose yield and production rate decreased with increasing reaction temperature from 28 to 108 C. The glucose yield versus time profile retained its characteristic sigmoidal profile. The reaction rate from 28 to 50 C decreased slowly away from the maximum at 28°C. In this temperature range, the maximum glucose yield remained at 2.7 to 2.9 millimole per gram of dry wood, and so no

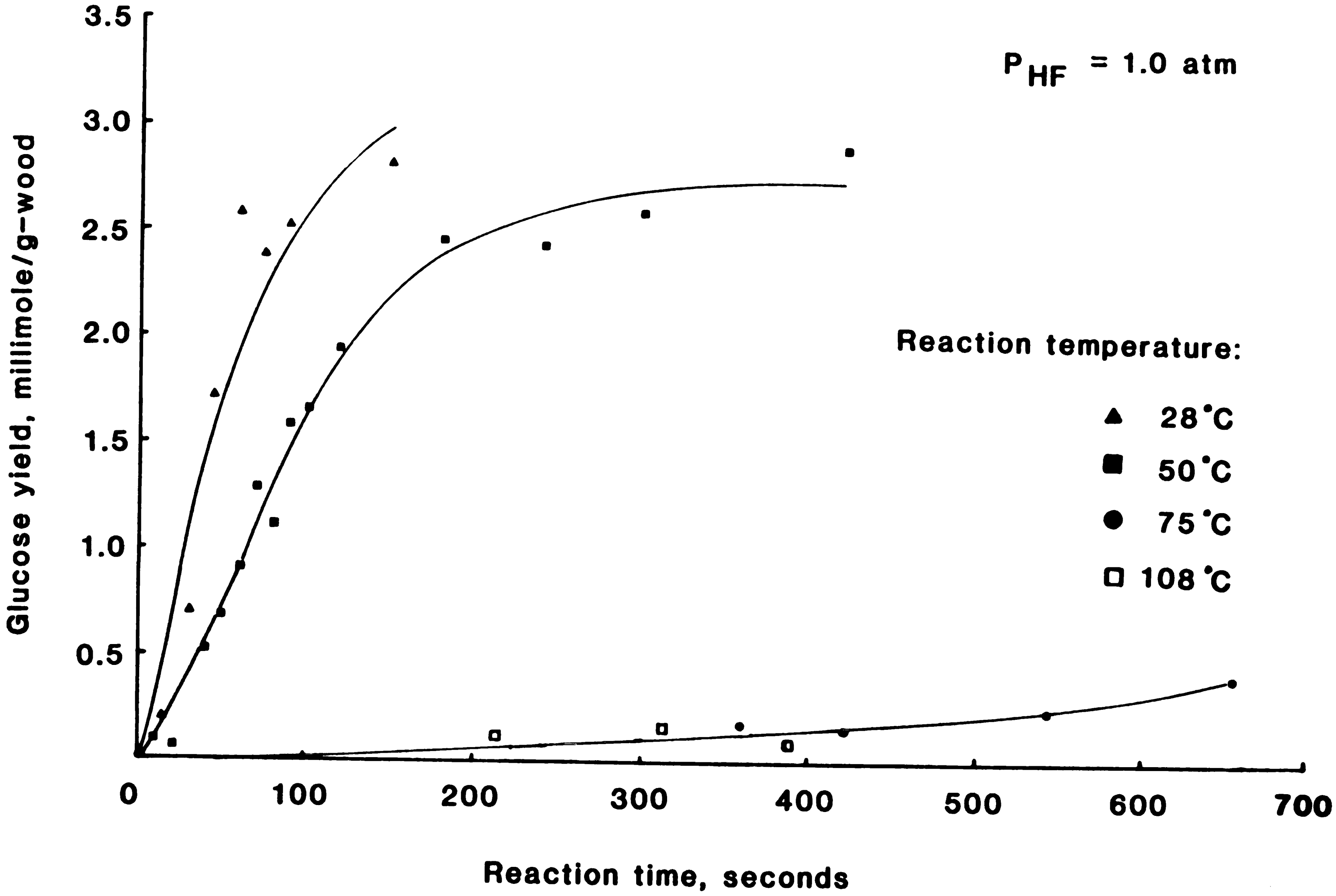

FIGURE 11. Glucose yield as a function of time for temperatures from 28°C to 108°C at an HF partial pressure of 1.0 atm.

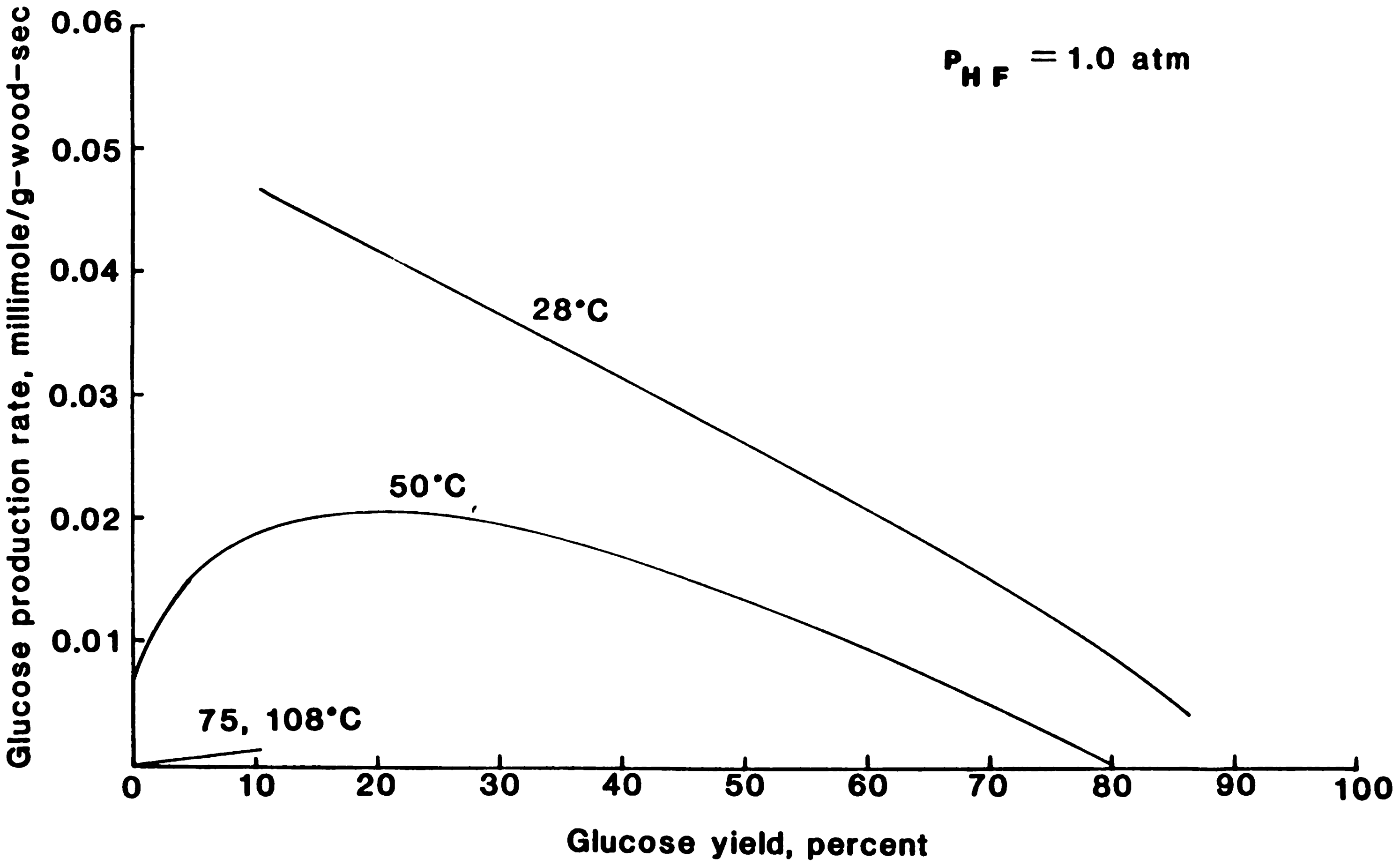

FIGURE 12. Glucose production rate versus glucose yield as a function of temperature from 28°C to 108°C at an HF partial pressure of 1.0 atm.

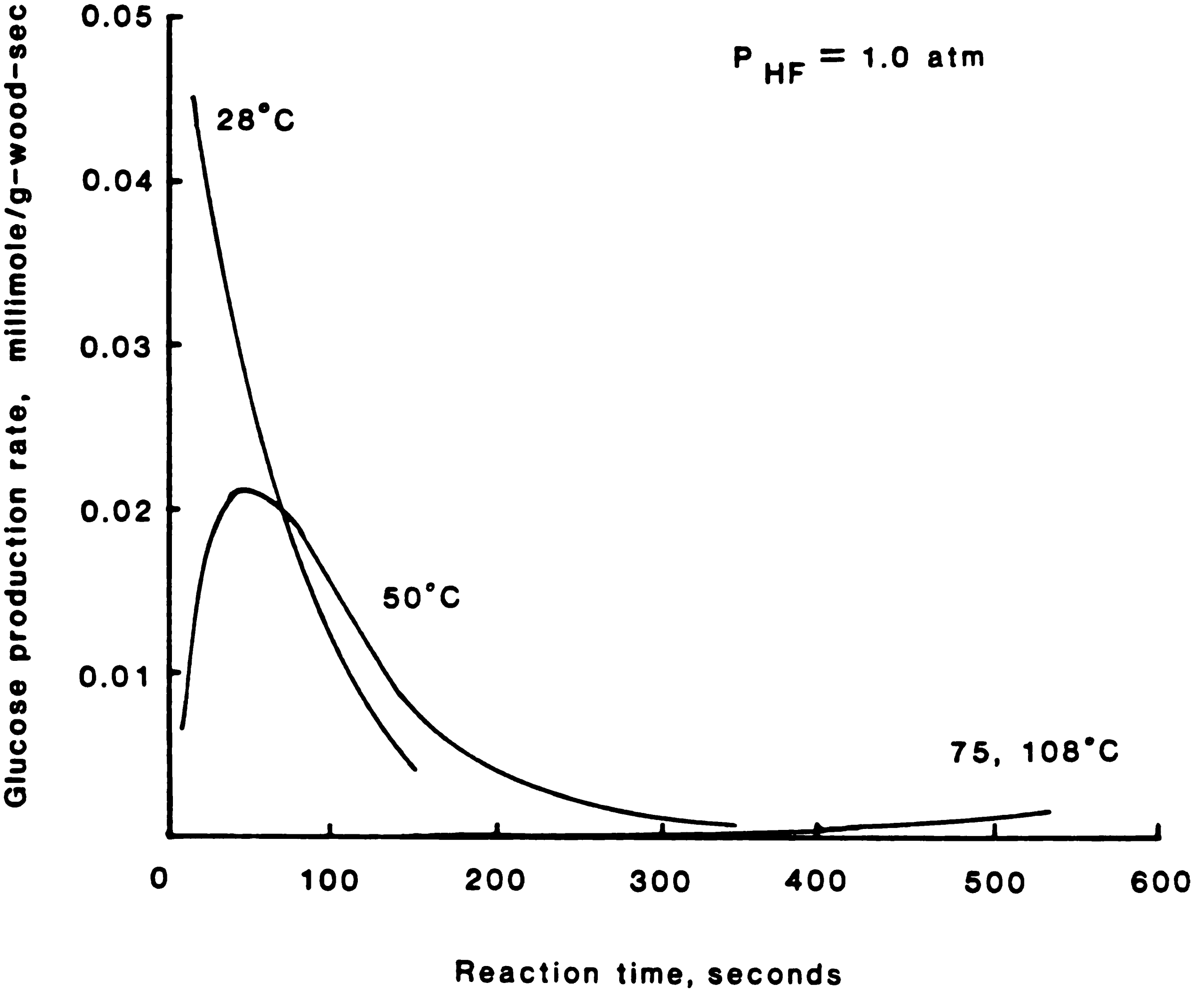

FIGURE 13. Glucose production rate as a function of time for temperatures from 28°C to 108°C at an HF partial pressure of 1.0 atm.

reaction product degradation occurred. From 50 to 75°C, the reaction rate dropped sharply, indicating a shift in rate control from cellulose solvolysis to some other process. At reaction temperatures greater than 50°C, the reaction rate was so slow that glucose yield-plateau data were not obtained within a experimentally-realistic reaction time, and so evidence for possible thermal reaction product degradation was not detected. The reaction rate from 75 to 108°C changed little and maintained a consistently low rate. Apparently, an intrinsic process other than cellulose solvolysis may have assumed control of the reaction rate.

Upon first inspection, the glucose production rate data seemed to contradict the Arrhenius equation. However, these rate data suggest that equilibrium-driven, heterogeneous rate processes may be coupled to the intrinsic cellulose-cracking reaction. Such processes may assume control of the overall intrinsic reaction rate at elevated reaction temperatures.

An example of an equilibrium-driven process is surface-adsorption of HF into the lignocellulosic matrix. It was observed that during the solvolysis reaction between cellulosic materials in wood and gaseous HF, the structure of the lignocellulosic matrix was retained and the solvolysis products appeared to "stick" to the lignin binder. Therefore, the ligoncellulosic matrix was available to provide sites for surface adsorption by HF molecules.

The rate of chemisorption for a heterogeneous reaction normally increases with increasing temperature. However, the physical adsorption isotherm decreases with increasing temperature. Surface adsorption of HF onto the lignocellulosic matrix prior to cellulose solvolysis could alter the overall intrinsic reaction rate, particulary if adsorption constants determined by a negative heat of adsorption are stronger functions of temperature than the rate constant for cellulose solvolysis. This speculation suggests that the overall intrinsic reaction rate could pass through an optimum in temperature. However, there is no direct experimental evidence to support such a conclusion with the data at hand.

Xylose yield versus reaction time data at 1.0 atm HF partial pressure for each reaction temperature are presented in Figure 14. In general, the xylose yield versus reaction time profile followed the same trend as previously described. In general, the time-dependent evolution of xylose decreased with increasing temperature, consistent with glucose yield versus time data at the same set of reaction conditions. However, for xylose yield data at 50° C, the xylose yield appeared to pass through a maximum in reaction time, indicating that some product degradation might have occurred during solvolysis. However, as mentioned earlier, the analytical procedures were not set up to detect for xylosyl degradation products.

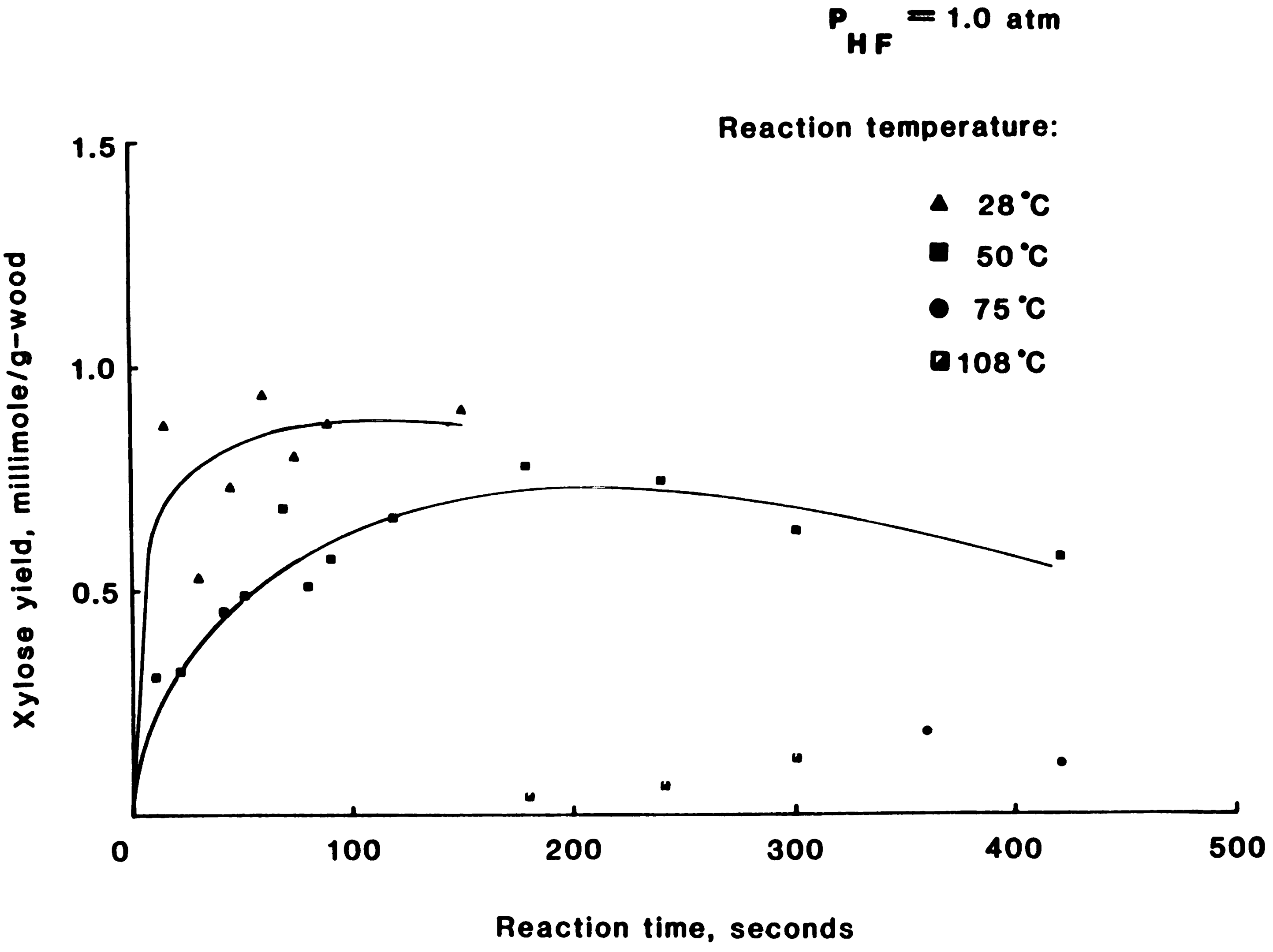

FIGURE 14. Xylose yield as a function of time from 28°C to 108°C at an HF partial pressure of 1.0 atm.

DISCUSSION AND CONCLUSIONS

The rapid reaction rates at ambient conditions and high sugar yields obtained from gas-phase HF saccharification of wood highlight the advantages of this process over liquid-phase HF saccharification and acid hydrolysis processes in general. It is desirable to develop reactor models for gas-phase HF saccharification of wood based on a fundamental, quantitative, intrinsic kinetic model for the solvolysis of cellulose in wood by gaseous HF. These reactor models can then be applied to reactor design and process optimization studies. In this way, gas-phase HF saccharification of wood can be more quantitatively assessed and compared to other biomass conversion technologies.

The first step toward development of a reactor model for gas-phase HF saccharification of wood is to generate intrinsic reaction rate data so that the intrinsic rate processes and chemical kinetic model can be elucidated. A detailed intrinsic kinetic model requires a physically representative reaction sequence and knowledge of rate-limiting steps. Further, the set of formulated rate equations must be solved in a form which can be fitted to glucose yield versus time data. In this way, chemical kinetic parameters (e.g., rate constants) for each rate process can be estimated. Once an intrinsic kinetic model has been developed, it can be modified to account for particle size and convective mass-transfer effects.

The complex reaction rate behavior exhibited by gas-phase HF saccharification of wood indicates that formulation of a quantitative rate model is premature if based solely on the rate data presented here. However, the rate processes which may determine the global reaction rate can be postulated from these data.

The Intrinsic Reaction Sequence

Reaction rate data for gas-phase HF saccharification of wood indicate that even in the absence of mass-transfer effects, heterogeneous rate processes are important. The sigmoidal profile of the glucose yield versus time data and the decrease of overall glucose production rate with increasing temperature suggest that surface interactions between vapor-phase HF molecules and cellulosic chains residing within the lignocellulosic matrix control the "cracking" of cellulose to glycosyl fluoride monomers. Logical candidates for the intrinsic rate processes of gas-phase HF saccharification of wood are summarized in Table 3. The intrinsic reaction scenario of Table 3 will now be described.

HF molecules in the pure vapor state exist as hyrogen-bonded hexomers at ambient temperature and pressure. Upon dilution in nitrogen, the hydrogen-bonded HF hexomer

Table 3. The intrinsic rate processes of gas-phase HF saccharification of cellulose in wood.

	Reaction	Process
1.	$(HF)_m\ (g) \overset{N_2}{\rightleftharpoons} HF\ (g) + (HF)_{m-1}\ (g)$	Depolymerization of HF upon dilution in N_2. $m \leq 6$.
2.	$[H\text{-}(G)_n\text{-}OH]_x\ (s) \overset{(HF)\ (g)}{\rightleftharpoons} x \cdot H\text{-}(G)_n\text{-}OH\ \ (s)$	Disruption of hydrogen-bonded linear cellulose chains within the microfibril. $n = 5000\text{–}10000$, $x = 40$ (typically).
3.	$H\text{-}(G)_n\text{-}OH\ \ (s) \overset{(HF)\ (g)}{\rightleftharpoons} H\text{-}\left(\underset{HF}{\underset{\cdot}{G}}\right)_n\text{-}OH\ \ (s)$ $S + (HF)_m\ (g) \rightleftharpoons (HF) \cdot S\ (s)$	HF adsorption onto the lignocellulosic matrix (S = surface site) and solvation of cellulose. Complete disruption of hydrogen-bonded HF.
4.	$H\text{-}\left(\underset{HF}{\underset{\cdot}{G}}\right)_n\text{-}OH\ \ (s) \longrightarrow H\text{-}(G)_{n-1}\text{-}OH\ (s) + H\text{-}G\text{-}F\ (s)$ $\longrightarrow H\text{-}(G)_i\text{-}OH\ (s) + H\text{-}(G)_j\text{-}F\ (s)$ $\longrightarrow n\ H\text{-}G\text{-}F\ (s) + H_2O$	Cellulose depolymerization (cracking). $n = i + j$.

Table 3. (continued).

Reaction	Process
5. $\text{H-G-F (s)} \xrightarrow[\text{fast}]{H_2O\ (1)} \text{H-G-OH (aq.)} + \text{HF (aq.)}$ $\text{H-(G)}_k\text{-F (s)} \xrightarrow{H_2O\ (1)} \text{H-(G)}_k\text{-OH} + \text{HF (aq.)}$	Hydrolysis of reaction products and regeneration of HF. Solid if $i > 6$, aqueous if $i \leq 6$.
6. $\text{H-(G)}_p\text{-OH (aq.)} + \text{H-(G)}_q\text{-OH (aq.)} \longrightarrow \text{H-(G)}_{p+q}\text{-OH (aq.)} + H_2O$ $\text{H-(G)}_p\text{-F} + \text{H-(G)}_q\text{-OH (aq.)} \longrightarrow \text{H-(G)}_{p+q}\text{-OH (aq.)} + \text{HF (aq.)}$	Reversion to water-soluble oligosaccharides. $p+q \leq 6$. α-1,6 linkage between p and q.
7. $\text{H-(G)}_{p+q}\text{-OH (aq.)} \xrightarrow{H^+\text{(aq.)}} (p+q)\ \text{H-G-OH (aq.)}$	Post-hydrolysis.

"depolymerizes" in the gas-phase, producing an oligomeric distribution of HF molecules of 1 to 6 monomer units in size. These HF molecules adsorb onto surfaces within the lignocellulosic matrix. Hydrogen-bonded linear cellulose chains (beta-1,4 polyglucan) make up the cellulose microfibril, which constitutes the bulk of the secondary cell wall in the lignocellulosic matrix. The hydrogen-bonded cellulose microfibril is "unraveled" by interactions with adsorbed HF molecules. These interactions may also reduce adsorbed, hydrogen-bonded HF molecules to monomeric HF.

The HF monomer fixes itself onto a glucan unit site on the cellulose chain and irreversibly "cracks" the beta-1,4 linkage at that site. The products of the solvolysis (cleavage) are two polyglucan (or single glucan) fragments, one of which is fluoridated at the 1-carbon on the terminal glucan unit of that fragment. Eventually, the cellulose molecule is completely cracked to alpha-D-glucopyranosyl fluoride monomers (10), which reside or "stick" on the lignocellulosic matrix. It is observed that the lignocellulosic matrix remains intact throughout the reaction, indicating that the solvolysis products are held in place by the lignin binder. Presumably, the lignin does not decompose or depolymerize in the presence of HF. Additionally, the reaction mixture was not agitated, and so no mechanical fragmentation of the sample occurred.

Finally, the chemistry of hydrolysis, reversion, and post-hydrolysis summarized by steps 5 to 7 in Table 3 are described elsewhere (10).

The intrinsic rate processes described by steps 1 to 4 in Table 3 may explain the complex reaction rate behavior exhibited by gas-phase HF solvolysis of cellulosic materials in wood. The nonlinear dependence of reaction rate on HF partial pressure is probably determined in part by the disruption of the HF hexomer in the vapor phase upon dilution in nitrogen. Such a phenomena could result in an effective HF partial pressure over the wood chip which is lower than the calculated HF partial pressure.

The decrease in overall glucose production rate with increasing reaction temperature is probably determined by physical adsorption of HF from the gas-phase onto the lignocellulosic matrix. The sigmoidal profile of the glucose yield versus time data may be determined by processes immediately preceeding cellulose solvolysis, such as HF-adsorption and hydrogen bond-breaking of cellulose microfibrils. As indicated earlier however, it is not certain which of these processes is rate-controlling.

Future Research

Future research of the chemical kinetics of gas-phase HF saccharification of wood will focus on unraveling the complex reaction rate behavior of this process and developing a quantitative rate model. The effect of HF concentration on the reaction rate will be determined by varying the total system pressure in the attempt to screen out the compounding effect of "HF-depolymerization" (via dilution of HF in nitrogen) on reaction rate. The effect of reaction temperature on reaction rate will be determined at a lowered HF partial pressure so that sub-ambient (less than 20 C) gas-stream temperatures can be achieved. In this expanded temperature range, it is anticipated that the reaction rate would pass through an optimum in temperature, indicating a shift from a reaction rate-controlling to an HF adsorption-controlling regime. Insitu gravimetric measurement of the HF uptake on wood will be used to study the HF adsorption isotherm on wood as a function of reaction time, temperature, and HF partial pressure. Internal mass-transfer effects will be explored and modeled by observing the effect of wood chip particle size on reaction rate. It is hoped that the results from all of these chemical kinetic experiments can be brought together to develop a fundamental rate model for gas-phase HF saccharification of wood.

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APPENDIX

Sugar Yield and Reaction Rate Data

Table 4. Sugar yield and reaction rate data.

HF partial pressure: 1.0 atm
Analysis method: GLC alditol-acetates, averaged over two assays

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
10	29.7	0.050	0.820
15	30.3	0.161	0.950
20	30.0	0.307	0.954
30	30.3	0.513	0.921
40	30.1	1.012	1.337
60	30.0	2.239	1.306
80	30.3	2.690	1.398
100	30.3	3.055	-
120	30.4	2.504	1.058
140	30.4	2.405	1.173
160	30.6	2.702	1.385
180	30.4	2.512	1.212
200	30.4	2.998	0.914
220	30.4	2.642	1.260

Table 4. (cont'd.).

HF partial pressure: 0.73 atm
Analysis method: GLC alditol-acetates, averaged over two assays

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
15	30.6	0.0	0.299
30	30.0	0.130	1.140
45	30.3	0.142	1.035
60	30.2	0.335	-
75	30.1	0.454	0.829
90	30.0	0.361	0.719
105	30.3	1.336	0.980
120	30.4	1.588	0.927
135	30.1	1.448	0.957
150	30.3	2.665	1.292
180	30.2	2.681	1.166
210	30.5	2.852	-
225	30.5	2.554	-
240	30.2	2.751	1.380
270	30.5	2.809	1.274

Table 4. (cont'd.).

HF partial pressure: 0.60 atm
Analysis method: HPLC

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
30	30.2	0.060	0.615
60	30.5	0.189	0.695
75	30.5	0.358	0.532
90	30.7	0.646	0.668
105	30.5	0.766	0.684
120	30.2	0.640	0.601
150	30.5	1.263	0.779
180	30.5	1.572	0.847
210	30.5	1.847	0.691
240	30.6	2.085	0.943
270	30.5	2.231	0.875
300	31.0	2.301	0.756
330	30.0	2.565	0.859
360	30.2	2.870	0.649
390	29.6	2.593	0.792
420	30.2	2.375	0.851

Table 4. (cont'd.).

HF partial pressure: 0.50 atm
Analysis method: HPLC

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
60	30.2	0.103	0.507
120	30.5	0.235	0.454
150	30.7	0.366	0.475
180	30.5	0.450	0.487
210	30.5	0.816	0.691
330	30.7	1.706	0.809
450	30.4	2.265	0.851
540	30.4	1.915	0.858
660	30.5	2.455	0.722
780	30.5	2.424	0.723

Table 4. (cont'd.).

HF partial pressure: 0.44 atm
Analysis method: HPLC

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
60	30.6	0.040	0.516
120	30.2	0.152	0.470
180	30.4	0.334	0.485
240	30.5	0.675	0.519
300	30.3	0.998	0.615
360	30.0	0.997	0.572
420	30.0	1.487	0.631
480	30.0	1.467	0.625
600	30.3	1.555	0.690
900	30.6	1.947	0.817

Table 4. (cont'd.).

HF partial pressure: 0.2 atm
Analysis method: HPLC

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
60	30.3	0.042	0.399
180	30.2	0.037	0.267
240	30.2	0.045	0.359
300	30.2	0.067	0.359
360	30.1	0.089	0.361
420	29.8	0.103	0.269
480	30.4	0.211	0.400
540	30.4	0.389	0.476
600	30.4	0.446	0.504
900	31.0	0.523	0.584

Table 4. (cont'd.).

HF partial pressure: 1.0 atm
Analysis method: HPLC

REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
10	50.0	0.095	0.302
20	49.4	0.063	0.333
40	49.8	0.522	0.458
50	50.4	0.690	0.492
60	50.3	0.905	0.492
70	50.5	1.281	0.679
80	50.5	1.122	0.508
90	50.4	1.574	0.565
100	50.5	1.667	0.654
120	49.9	1.943	0.659
180	50.5	2.445	0.767
240	55.4	2.429	0.742
300	55.8	2.580	0.627
420	55.8	2.899	0.567

Table 4. (cont'd.).

HF partial pressure: 1.0 atm
Analysis method: HPLC

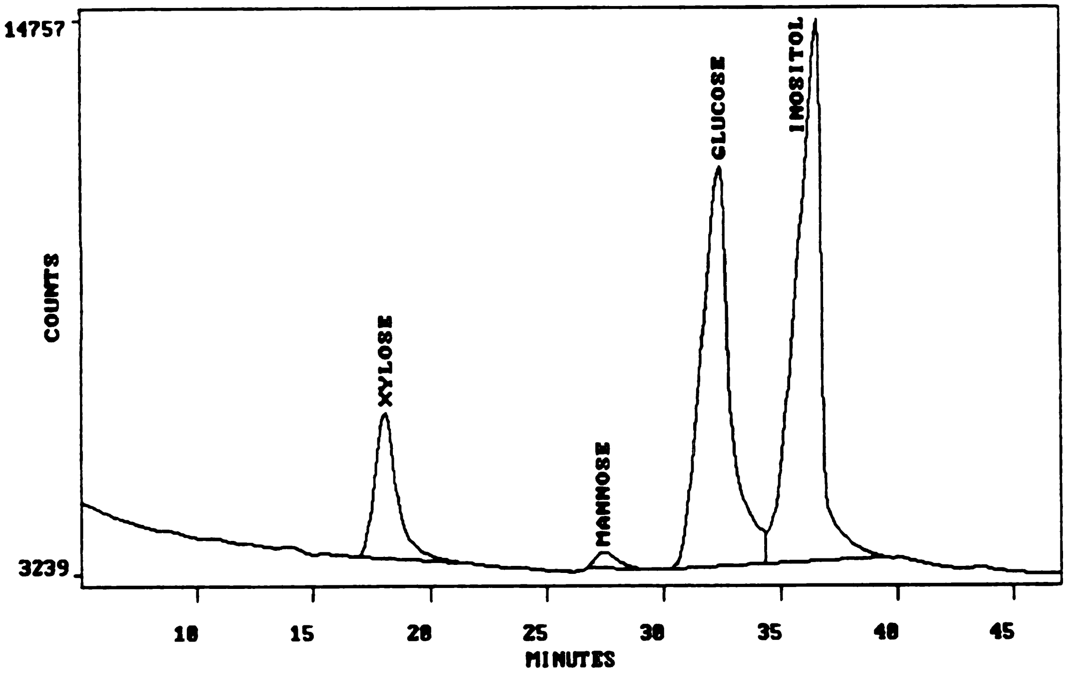
REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
15	27.6	0.207	0.830
30	27.5	0.697	0.527
45	27.6	1.171	0.729
60	26.6	2.579	0.939
75	28.4	2.384	0.795
90	28.6	2.515	0.861
150	28.6	2.813	0.898

Table 4. (cont'd.).

HF partial pressure: 1.0 atm
Analysis method: HPLC

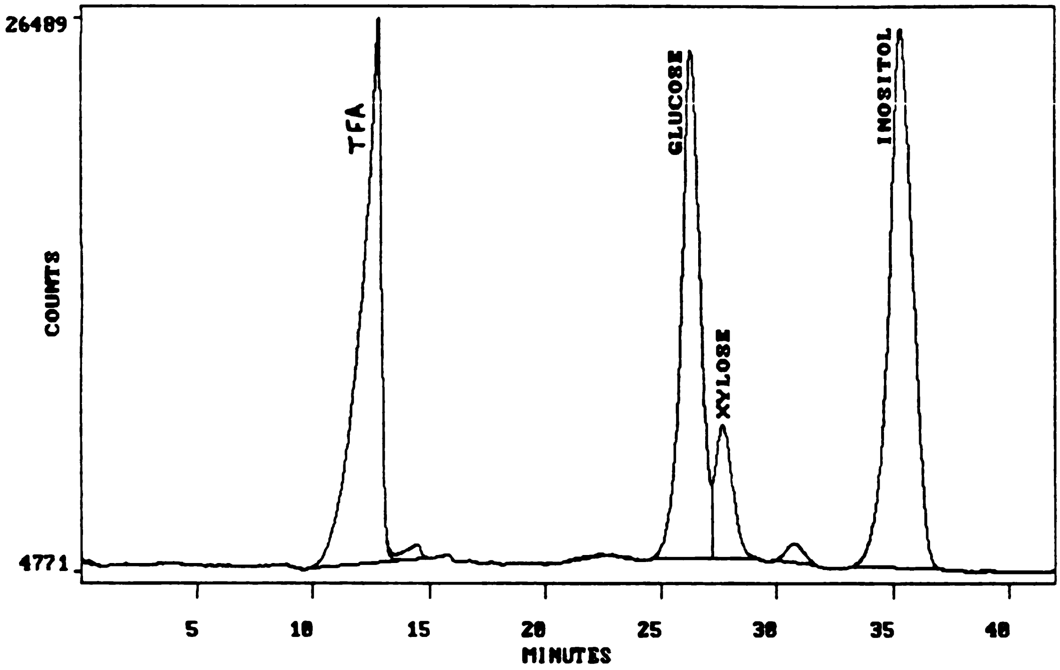
REACTION TIME (sec)	TEMPERATURE (°C)	GLUCOSE YIELD (mmol/g-wood)	XYLOSE YIELD (mmol/g-wood)
360	75.2	0.194	0.180
420	75.2	0.157	0.108
540	74.7	0.261	0.114
660	74.7	0.402	0.179
180	108.8	0.0	0.035
240	108.9	0.055	0.061
300	108.1	0.125	0.120

Sugar Chromatography



Analysis method: GLC-alditol acetates/Internal Standard
Sample description: sugars from HF-hydrolyzed Bigtooth Aspen. Reaction conditions: 180 sec, 30.4°C, HF partial pressure of 1.0 atm.
Injection volume: 1.5 μl
Carrier gas: helium at 40 cc/min
Temperature program: initial temperature of 130°C; 1°C/min for 50 min
Column: PEGS-224
Detector: flame ionization (FID)

Gas-liquid chromatography of water-soluble monomer sugar yields obtained from gas-phase HF solvolysis of Bigtooth Aspen.



Analysis method: HPLC/Internal Standard
Sample description: sugars from HF-hydrolyzed Bigtooth Aspen. Reaction conditions: 75 sec, 28.4°C, HF partial pressure of 1.0 atm.
Injection volume: 50 μl; ca. 400 μg total sugar plus standard
Mobile phase: doubly-distilled, deionized, degassed water
Flowrate: 0.6 ml/min
Temperature program: isothermal at 85°C for 42 min
Column: Biorad Aminex 42A and 87P in series
Detection: Refractive index (RI)

note: TFA peak due to incomplete evacuation of post-hydrolysis acid residue.

High-performance liquid chromatography of water-soluble monomer sugar yields obtained from gas-phase HF solvolysis of Bigtooth Aspen.