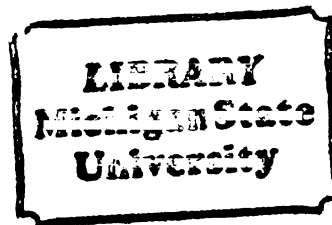


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HYDROGEN FLUORIDE SACCHARIFICATION

presented by

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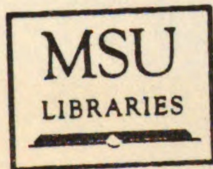
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PRELIMINARY INVESTIGATIONS OF GAS PHASE

HYDROGEN FLUORIDE SACCHARIFICATION

PRELIMINARY INVESTIGATION

HYDROGEN FLUORIDE SACCHARIFICATION

By

Kevin W. Downey

Kevin W. Downey

Hydrogen fluoride (HF) is a new technology for the production of fuels and chemicals. It possesses several advantages over competing processes: high reaction rates, and acid recycle.

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1985

any HF partial pressure dependence was subsequently found to be negligible. The reaction process was simplified to adequately model the reaction process. The results in the production of first order reaction rate were due to

368-5299

progressively form more monomer, just the opposite of what is found for liquid phase HF reaction.

ABSTRACT

PRELIMINARY INVESTIGATIONS OF GAS PHASE HYDROGEN FLUORIDE SACCHARIFICATION

By

Kevin W. Downey

Hydrogen fluoride (HF) saccharification is a relatively new technology for the conversion of lignocellulosics to fuels and chemicals. It possesses significant advantages over competing processes in regard to sugar yields, reaction rates, and acid recycle requirements, resulting in impressive economic potential. In an effort to improve the HF saccharification data base, a preliminary investigation of the gas phase HF/wood reaction kinetics and a qualitative investigation of the polymeric sugar reaction product distribution were performed. A first-order model neglecting any HF partial pressure dependence was originally assumed for both glucose and xylose production. The model was subsequently found to be acceptable for xylose but too simplified to adequately model the glucan-to-glucose reaction process. The gas phase HF/wood reaction results in the production of first large polymers which break down to

progressively form more monomer, just the opposite of what is found for liquid phase HF reaction.

ACKNOWLEDGEMENTS

Research is not the result of a single effort but rather a combination of efforts from many individuals. This paper is no exception. Without the help of the following, this work is dedicated to my Mother, gone and Dr. Martin C. yet ever-present. I miss her so very much. My stay at Michigan State University. He proved to be more than a mere advisor. In addition, I would like to thank Dr. Derek Lamport, Dr. Susan Selke, and Greg Barber for their assistance and valued friendship. In conclusion, I would like to express my gratitude and appreciation to Gayle, without whose encouragement and support I would never have come to MSU.

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emphasis has been placed on coal conversions as a means of replacing or supplementing oil. However, because coal is a finite resource, its conversions will not be useful indefinitely. A renewable INTRODUCTION is therefore needed to ensure that the necessary fuels and chemicals will be

avail. With renewed conflict in the Middle East, attention has again been focused on crude oil and its continued supply to the Western World. Though problems with oil transportation have presently take precedence over problems with the actual finite oil supply, it is only a question of time before the recession-induced surpluses dwindle and alternatives to oil are investigated anew. Because crude oil is a finite resource, these alternatives will be necessary in the long run and probably desirable in the short run. Therefore, the ground work must be established for new energy sources in order that an orderly transition to these new supplies can be made when oil does indeed run out. Also, these new supplies can be beneficial in the short run by lengthening the crude oil lifetime.

Following World War II, cheap crude oil from North Africa and the Middle East was plentiful. This contributed to the rapid industrial expansion of the post-war world. Scarcely a thought was given to oil supplies until 1973 when the Arab oil embargo showed just how dependent the United States and the rest of the Western World was on foreign oil. The result of this oil shortage was a renewed interest in alternative sources of liquid fuels and chemicals. Much

emphasis has been placed on coal conversions as a means of replacing or supplementing oil. However, because coal is a finite resource, its conversions will not be useful indefinitely. A renewable resource is therefore needed to ensure that the necessary fuels and chemicals will be available in perpetuity. Though nuclear energy is renewable via the Breeder Reactor, it cannot supply the required array of fuels and chemicals, and its safety has proven to be a difficult problem to overcome. The logical choice as a conversion feedstock is therefore lignocellulose. Lignocellulosic materials are renewable indefinitely and are capable of supplying a wide range of fuels and chemicals. A relatively new example of a lignocellulose-conversion technology is hydrogen fluoride (HF) saccharification of wood. Use of the very favorable early results, research is continuing. HF saccharification has proven to possess significant advantages over competing conversion technologies. Among these are quick reaction times, high sugar yields, and an efficient acid recycle. However, because of its fairly recent emergence, HF saccharification technology requires a great deal more research before a final determination of its merits can be performed. In this work, the preliminary economics and kinetics of gas phase hydrogen fluoride saccharification are investigated. This research, and that to follow, will ultimately aid in future process designs and HF technology applications.

Sugar yields of approximately 90% of theoretical were achieved (11,12).

Work at Michigan State University began in 1979 as a result of work PAST AND PRESENT RELATED RESEARCH

Laboratory. HF was being used to extract the cellulose

fract Extensive practical investigations of HF (hydrolysis).

saccharification were begun in Germany in the 1930s by Fredenhagen and Cadenbach (6) though the effects of HF on cellulose had been noted much earlier (7). However, the second world war erased much of this early research.

Following World War II, very little had been done on this topic until 1979 when several researchers independently and began to investigate HF saccharification anew. (In the 1950s, the topic was briefly studied in Russia (8,9).) Because of the very favorable early results, research continues worldwide on various aspects of HF technology.

In 1929, Helfrich and Bottger investigated the reaction of HF with cellulose (10). The aforementioned Fredenhagen and Cadenbach discovered that a glucosyl fluoride intermediate was formed. Upon addition of water, this intermediate released HF and glucose. Thus, the HF was released, acting much like a catalyst. They later applied their research on both liquid and gas phase HF studies where sugar yields of up to 95% of theoretical were obtained (6). The research was continued in 1937 by Hoch and Bohunek who built a pilot plant using gas phase HF under low pressure.

Sugar yields of approximately 90% of theoretical were achieved (11,12). (14). An important result concerning lignin Work at Michigan State University began in 1979 as a result of work being done at the MSU Plant Research Laboratory. HF was being used to extract the cellulose fraction from various cell wall proteins (deglycosylation). The idea then evolved that HF would be a good means of converting cellulose and lignocellulosics to sugar. Soon after, investigations began in collaboration with the MSU Department of Chemical Engineering. At MSU, work to date has concentrated on liquid phase saccharification studies with a major emphasis on yields and kinetics. Selke has extensively investigated these topics and has proposed a pseudo-first-order reaction model which fits the data fairly well if an "initial delay" parameter is included. This parameter is viewed as accounting for the time required for solubilization of the wood samples (4,13). Computer analyses of the data allowed calculations of first order rate constants as well as activation energies (4,13).

In addition to work at MSU, work on HF saccharification continues in France, Germany, Canada, and Denmark. In France, Defaye et al are investigating fundamental solution chemistry and lignin characterization. The glucosyl and xylosyl fluorides formed have been found to be in a concentration-dependent equilibrium with oligomeric reversion products. The α -D-glucopyranosyl fluoride predominates in dilute solutions while the xylose/xylan

equilibrium lies virtually completely on the side of the reversion products (14). An important result concerning lignin is that HF lignin appears to be even more condensed than comparable H_2SO_4 and HCl lignins (14). Previously, HF lignin was thought to be of significantly superior quality. In Germany, Hoechst is investigating the practical implementation of a gas phase HF saccharification process with special emphasis on adsorption properties (15). The general process advocated by Hoechst is different from most others in that it contains a prehydrolysis of the wood substrate, thus removing the hemicellulose fraction as well as other impurities. Though benefits result from the prehydrolysis step, its ultimate merit will have to be decided economically. In Canada, Canertech is studying practical applications of vapor phase HF hydrolysis. The Canadians hope to have a pilot plant operating in the near future (16). Danish researchers are also studying practical applications of vapor phase HF saccharification but with barley straw as the principal cellulose source (17).

With the contributions of the above researchers as well as others who may join in their investigations, it is only a question of time before HF saccharification attains its rightful place as a commercially viable technology. They all have three principle components: cellulose, hemicellulose, and lignin. Included with these are a small amount of ash and extractives. Table 1 shows the composition of several lignocellulosics in regards to the three principal

TABLE 1

Biomass Content

(J. P. Bartholic, et al, in E. Solter (Ed.), Wood and Agricultural Residues, Research on Use for Food, Fuels, and Chemicals)

LIGNOCELLULOSE COMPOSITION AND AVAILABILITY

The composition of lignocellulosics is very complex.

With the proper technology, only a minimum of conversion need take place to yield even fairly complex chemicals such as phenolics. In fact, 95% of our necessary synthetic polymers can be derived from lignocellulose (1). However, at present much of the technology necessary to usher in the age of widespread lignocellulose-derived fuels and chemicals is still in the developmental stage, though significant progress is being made.

Though various crude oils differ in composition depending on the part of the world they originate from, they are not nearly as diverse as are the compositions of different lignocellulosics. This fact tends to hamper the development of the needed technology because vastly different processes may be required for different lignocellulosic substrates, unlike the relatively small changes necessary when crude oil feedstocks are changed. Although plants do vary extensively in composition, they all have three principle components: cellulose, hemicellulose, and lignin. Included with these are a small amount of ash and extractives. Table 1 shows the composition of several lignocellulosics in regards to the three principal

components (2). The particular lignocellulosic chosen for a given conversion will depend on the desired end product.

(J. F. Bartholic, et al, in E. Soltes (Ed.), Wood and Agricultural Residues, Research on Use for Feed, Fuels, and Chemicals, New York, 1983, pp. 543-544.

Biomass	Cellulose Content (%)	Hemicellulose Content (%)	Lignin Content (%)
Barley	Str 41.9	E 44.27-5.66 Hu 27.0-30.1	16-22
Corn	Sta 34.4 C 34.9	Sta 23.7 C 37.3	Sta 10.5 C 7.4
Sorghum	Sto 39.6	Str 25	H 13.6
Hay (loose)	A 35	Str 25	A 7.3
Oats	Str 49.3	Str 25	Str 14-22
Rye	Str 41.7	Str 24	
Soybeans	Sto 46.3	Str 25	H 11-4 Hu 6.5
Wheat	Str 47.0	Str 25	Str 13.9
Wood			
Hardwood	45.8	30.7	20.3
Softwood	43.8	24.5	29.5

A-All hay types combined E-Endosperm Hu-Hull Sto-Stover
C-Cob the raw material H-Hay stalk Sta-Stalk Str-Straw

therefore be a tradeoff between plant size (capital costs) and collection and transportation costs. Unlike crude oil refineries which are widely scattered and very large, the optimum or best-case scenario for lignocellulose conversions will involve many sites scattered within a given area. Though virtually any living plant can potentially be a feedstock for fuel and chemical production, its suitability only

components (2). The particular lignocellulosic chosen for a given conversion will depend on the desired end product. For example, plants high in lignin content will be ideal for the production of phenolics, whereas plants high in the cellulose content will be better used for the production of glucose and glucose-derived chemicals.

Once a particular feedstock has been chosen for a conversion process, thought must be given to the available supply of that feedstock. Because different lignocellulosics are confined to definite areas of the country, conversion plants will need to be geographically consistent. Thus, softwood conversion plants will need to be located in the Northwest, Southeast, or Maine, for these areas contain the highest softwood concentration. In a similar fashion, plants utilizing corn residues must be located in the Midwest.

Because collection and transportation costs will be quite high for these lignocellulose conversion plants, the plants must be sufficiently small to allow minimal costs for getting the raw material to the facility. There will therefore be a tradeoff between plant size (capital costs) and collection and transportation costs. Unlike crude oil refineries which are widely scattered and very large, the optimum or best-case scenario for lignocellulose conversions will involve many sites scattered within a given area. Though virtually any living plant can potentially be a feedstock for fuel and chemical production, in reality only

a few are feasible because of their relative abundance and centralization. These include hardwoods, softwoods, corn residues, and wheat residues. Of these, hardwoods and softwoods would be the easiest to process because of the high cellulose concentration.

Before expensive pilot plant or laboratory work is done, it is important to investigate process economics to determine whether or not the conversion in question is feasible. The economics can be used as a barometer to justify continued research or project termination. For this reason, the economics for a proposed 10 MM gal/year ethanol plant utilizing either liquid or gas phase hydrogen fluoride saccharification were estimated using a wood feedstock (3). The particular wood in question was Sigttooth Aspen (Populus grandidentata).

In deriving the economics, detailed designs were performed for both liquid and gas phase HF saccharification systems. These systems were then coupled to a conventional fermentation scheme (3). The differences between the gas and liquid phase HF ethanol plants result then from the saccharification portion alone; all else is identical. Because of the scarcity of technical information regarding HF saccharification, a great deal of assumptions were necessary. Therefore, the reported numbers should be taken as rough estimates. However, the goal of the study was merely to see whether or not the process warranted continued research, and this goal was easily satisfied. Table 1 shows

TABLE 2
Manufacturing Cost and Profitability Buildups
for Base Case in 1982 Dollars*

(K. Downey, S. Selke and M. Hawley, in Proceedings of the Seventh International PPRS Industrial Wood Energy Forum, Nashville, PRELIMINARY HF SACCHARIFICATION ECONOMICS.)

	Liquid Phase	Gas Phase
Fixed (No Control Equipment)	15,585,000	8,330,000
Control Fixed Capital		117,000
Before expensive pilot plant or laboratory work is done, it is important to investigate process economics to determine whether or not the conversion in question is feasible. The economics can be used as a barometer to justify continued research or project termination. For this reason, the economics for a proposed 10 MM gal/year ethanol plant utilizing either liquid or gas phase hydrogen fluoride saccharification were estimated using a wood feedstock (3). The particular wood in question was Bigtooth Aspen (<u>Populus grandidentata</u>).	15,702,000	8,447,000
Other Chemicals (H ₂ SO ₄)	670,000	670,000
Wood	4,922,000	4,922,000
Supervision, Overhead, Eng.,		
Fixed Capital	3,455,000	1,312,000
	1,091,000	583,000
TOTAL MANUFACTURING COST	13,314,000	11,742,000

In deriving the economics, detailed designs were performed for both liquid and gas phase HF saccharification systems. These systems were then coupled to a conventional fermentation scheme (3). The differences between the gas and liquid phase HF ethanol plants result then from the saccharification portion alone; all else is identical. Because of the scarcity of technical information regarding HF saccharification, a great deal of assumptions were necessary. Therefore, the reported numbers should be taken as rough estimates. However, the goal of the study was merely to see whether or not the numbers justify continued research, and this goal was easily satisfied. Table 2 shows

the major results of the analysis (3). As
 TABLE 2
 Manufacturing Cost and Profitability Buildups
 expected, the for Base Case in 1982 Dollars*

(K. Downey, S. Selke and M. Hawley, in Proceedings of the Seventh International FPRS Industrial Wood Energy Forum, Nashville, Tennessee, September 19-21, 1983, in press.)

	Liquid Phase	Gas Phase
Fixed Capital Investment (No Control Equipment)	15,585,000	8,330,000
Control Fixed Capital (5% of Above)	779,000	417,000
TOTAL FIXED CAPITAL INVESTMENT	16,364,000	8,747,000
Manufacturing Costs (Annual)		
HF	363,000	363,000
Other Chemicals (H ₂ SO ₄)	670,000	670,000
Utilities	2,763,000	2,842,000
Wood	4,922,000	4,922,000
Labor	1,050,000	1,050,000
Supervision, Overhead, Eng., Maint. (15% of Total Fixed Capital)	2,455,000	1,312,000
Depreciation	1,091,000	583,000
TOTAL MANUFACTURING COST	13,314,000	11,742,000
Revenues (Annual)		
Ethanol	18,200,000	18,200,000
Xylose Syrup	4,282,000	4,282,000
Lignin	2,706,000	2,706,000
TOTAL REVENUES	25,188,000	25,188,000
Net Income Before Tax	11,874,000	13,446,000
Net Income After Tax (48% Tax Rate)	6,174,000	6,992,000
Depreciation	1,091,000	583,000
Cash Flow/Year	7,265,000	7,575,000
Return on Investment (After Tax)	37.7%	79.9%

*Base case assumes 15 year plant lifetime, zero salvage value, straight-line depreciation. For other assumptions, see original text.

the major results of the economic analysis (3). As expected, the ethanol plant using gas phase HF is much more profitable than the liquid phase design, resulting principally from quicker reaction times (giving lower reactor capital costs) and lower cooling requirements.

Another important feature of the economics concerns the sensitivity analysis. The economics do not appear to be very sensitive to either raw wood (Populus grandidentata) cost or HF cost, assuming the given HF recycle efficiency of 99.5%. The most important cost affecting the economics appears to be the selling price of ethanol (3). Though a great deal of research needs to be done before reliable economic data can be generated, at present the numbers appear very promising. (For a complete analysis of the economics, please consult the original reference of Downey et al. (3).)

Enzymatic processes have the advantage of requiring only ambient operating conditions and producing a pure product but also have the disadvantages of relatively low yields, long reaction times, and expensive enzyme costs (18).

HF saccharification combines the benefits of ambient operating conditions, short reaction times, and very high sugar yields. In addition, acid recycling will be easier, principally due to the low boiling point of HF compared to that of HCl and H_2SO_4 . Recycle efficiencies of 99-99.9% of theoretical have been reported by several investigators.

(15,16,17). Because of the above advantages, HF saccharification appears to be the method of choice for the production of liquid fuels and chemicals from

lignocellulose COMPARISON OF ALTERNATIVE TECHNOLOGIES

Competing with HF saccharification are various hydrolysis processes. The major products from each of these are simple sugars. These processes fall into three general categories: concentrated acid, dilute acid, and enzymatic processes.

Concentrated acid processes have short reaction times, ambient operating conditions, and higher sugar yields than dilute acid or enzymatic hydrolyses. However, they also have severe corrosion problems and a condensed lignin byproduct. Dilute acid processes are fairly cheap and have short reaction times but require high temperature and pressure and give yields on the order of only about 50%. Enzymatic processes have the advantages of requiring only ambient operating conditions and producing a pure product but also have the disadvantages of relatively low yields, long reaction times, and expensive enzyme costs (18).

HF saccharification combines the benefits of ambient operating conditions, short reaction times, and very high sugar yields. In addition, acid recycling will be easier, principally due to the low boiling point of HF compared to that of HCl and H_2SO_4 . Recycle efficiencies of 98-99% of theoretical have been reported by several researchers

(15,16,17). Because of the above advantages, HF saccharification appears to be the method of choice for the production of liquid fuels and chemicals from lignocellulosic feedstocks.

In its virgin state, lignocellulose is a very complex substrate. Though cellulose is the major component, various amounts of hemicellulose, lignin, ash, and extractives are also present. The composition of the standard Bigtooth Aspen tree (*Populus grandidentata*) used in our studies is as follows (4):

Component	% of Dry Wood
Cellulose	50
Hemicellulose	29
Lignin	15.3
Extractives	4
Ash	2.7

Glucan is present in not only the cellulose fraction but the hemicellulose fraction as well. After residues in only the hemicellulose portion. On a dry gram basis, our standard tree contains 3.8 x 10⁻³ moles glucan and 1.4 x 10⁻³ moles xylan (4).

As the HF vapors contact the wood, the following reaction takes place forming glycosyl fluorides (Xylosyl-flourides are formed in a similar manner).



The HF vapors adsorb onto the surface of the wood chip then diffuse through the wood pores, moving along the HF concentration gradient. The formation of sugar fluorides

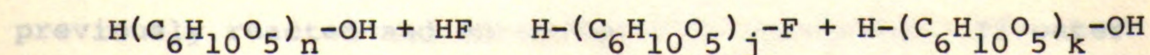
SIMPLIFIED REACTION PROCESSES AND MODELING lignin matrix which forms a network throughout the chip. For this

In its virgin state, lignocellulose is a very complex substrate. Though cellulose is the major component, various amounts of hemicellulose, lignin, ash, and extractives are also present. The composition of the standard Bigtooth Aspen tree (Populus grandidentata) used in our studies is as follows (4):

<u>Component</u>	<u>% of Dry Wood</u>
Cellulose	50
Hemicellulose	29
Lignin	16.6
Extractives	4.1
Ash	0.3

Glucan is present in not only the cellulose fraction but the hemicellulose fraction as well, while xylan resides in only the hemicellulose portion. Overall, on a per gram basis, our standard tree contains 3.441×10^{-3} moles glucan and 1.4×10^{-3} moles xylan (4).

As the HF vapors contact the wood sample, the following reaction takes place forming glucosyl fluorides. (Xylosyl fluorides are formed in a similar fashion.)



where $j + k = n$

The HF vapors adsorb onto the surface of the wood chip then diffuse through the wood pores, moving along the HF concentration gradient. The formation of sugar fluorides will be hampered somewhat due to the presence of the lignin matrix which forms a network throughout the chip. For this reason, reaction rates for cellulose (having no lignin matrix) are higher than for wood. Hydrogen fluoride will be consumed by the sugar fraction reacting with the HF and by lignin fluoridation (to a small degree) and fluoride salt formation. The fluoride salt losses result from reaction with the ash component composed principally of calcium, the potassium, and magnesium salts(4). In the liquid phase HF/wood reaction, the wood structure is broken down by the formation of sugar fluorides at the surface. The chip dissolves as the sugar fluorides slough off of the chip and mix with the bulk fluid. On the other hand, with reaction in the gas phase, the reaction products remain in solid form though the chip structure does break down substantially. Diffusion of HF occurs through wood already exposed to HF. If the reaction rate is viewed as being virtually instantaneous, then diffusion will only occur through previously reacted material. However, if mass transfer rates and reaction rates are both considered to be important, then diffusion of HF will occur through both previously reacted and unreacted wood substrate. If water is present (these initial studies were all done with partial anhydrous wood samples), then its diffusion direction will

depend on the relative water concentrations in the wood and the vapor stream. Since HF becomes more corrosive in the presence of water, the vapor stream was and probably should remain water-free unless proper materials are used. Corrosion-resistant materials such as monel will, however, significantly increase the cost of both bench-scale tests and future plant construction.

Initially, temperatures to be investigated for gas phase HF saccharification were on the order of 100°C . However, due to equipment limitations, these temperatures were scaled down considerably. At higher temperatures, the reaction rates would most likely be very high causing mass transfer limitations to prevail. The samples were, therefore, meticulously prepared of exact thickness to facilitate the derivation of a diffusion coefficient. However, early results caused a shift in the proposed relative importance of the rate processes. For reasons that will be discussed later, it became apparent that mass transfer limitations were not important, at least with the small wood sample size investigated. As with the liquid phase studies, the reaction rate appears to be the limiting process.

Because the gas phase process appeared to be reaction rate limiting, as were the liquid phase studies, an analogous model was initially proposed for the reaction of HF with wood. This model neglects the effects of HF partial pressure, i.e., the soon-to-be-derived rate constants and

activation energies are independent of HF partial pressure, or very nearly so. The pseudo-first-order reaction model of Selke (4) was proposed to fit the gas phase HF system. All intermediates are neglected. Integration of the first order rate expressions for glucose and xylose yield the following:

$$C_c = C_{c_o} e^{-kt} , C_H = C_{H_o} e^{-kt}$$

where C_c = concentration of cellulosic glucan

C_{c_o} = initial concentration of cellulosic glucan

k = rate constant

t = time

C_H = concentration of hemicellulosic xylan

C_{H_o} = initial concentration of hemicellulosic xylan

The rate constant is itself expressed as a function of temperature of the form:

$$k = k_o \exp \left[- \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right]$$

where k_o = reference temperature rate constant

E_a = activation energy

R = ideal gas constant

T = temperature

T_o = reference temperature

The data given in the following section is based upon this

simplified first-order model. A more complex system

including HF partial pressure dependence is discussed later

in this paper, and accompanying calculations are given.

satisfactory, but several factors must be considered.

will certainly be obtained as a result of these early studies.

The acquisition of yield and rate data will make possible a reliable reEXPERIMENTAL WORK necessary for practical industrial applications of the technology. Fundamental yields and rate data Goals of the Program the improvement or rejection of the models formulated to simulate the HF/wood react Investigations of HF saccharification have continued at Michigan State University for several years. However, proved studies have concentrated on liquid phase HF, and this paper represents our first true effort toward vapor phase HF for saccharification research. Consequently, the overall goals of these "first pass" preliminary investigations were to elucidate as much as possible about basic yields and kinetics of the process. In addition to the actuality of laboratory work, it was our goal to investigate the economic aspects of the process in order to determine if there is justification in continuing the research, for the economics will ultimately decide the future of the technology.

Because these results represent an initial effort, they must be viewed as preliminary in nature. The goal was not necessarily to derive irrefutable data, but rather to obtain early results such that improvements and new experimental procedures could arise from the inevitable inefficiencies encountered in the initial system design. This is not to say that the data obtained was in any way less than satisfactory, but rather that new and more extensive data

will certainly be obtained as a result of these early studies.

The acquisition of yield and rate data will make possible a reliable reactor design, necessary for practical industrial applications of the technology. Fundamental yields and rate data will also facilitate the improvement or rejection of the models formulated to simulate the HF/wood reaction processes. Initially, it was thought that mass transfer limitations would prevail, but early results proved this assumption to be false, and the views were subsequently changed. This last thought will be discussed in greater detail in the following sections of this paper.

By viewing the yield, kinetics, and economic data as well as the input of researchers worldwide, the overall merit of the HF saccharification process, specifically of the gas phase HF system, can be evaluated. Though a final determination still awaits, it appears that HF saccharification will be an important facet of the long term biomass-to-fuels-and-chemicals technology.

in. were then taken. The shavings were finally sectioned into approximately $3/8"$ x $3/8"$ squares. The thin samples were deemed necessary in order to minimize end effects during reaction. The Sample Preparation sample preparation technique was a collection of very flat, regular,

Before the gas phase HF saccharification studies began, it was believed that the reaction process may be mass transfer limited instead of reaction rate limited as was the case in the liquid phase studies (4,5). With this in mind, special care was taken to prepare wood samples for gas phase HF investigations. One problem which was initially difficult to overcome was the fact that the standard tree used in all HF studies to date had been completely chipped. Had large branches or such been unchipped, it would have been quite easy to plane these down to a desired width. The thin sheet could then have been sectioned as desired. However, because only wood chips were available, a new strategy was required. Chips of approximately $1-1/2"$ x $1"$ x $1/2"$ were sanded on one side using a commercial hand drill sander and attached in succession onto a length of $2"$ x $2"$ board. The sanding was necessary due to the initially very irregular nature of the chips. The $2"$ x $2"$ board was then sectioned between chips leaving single chips mounted on approximately $2"$ x $2"$ x $2"$ support cubes. These cubes were then mounted on a microtome apparatus used for preparing thin wood slide samples. The mounted wood chips were planed to a flat, uniform surface. Shavings on the order of 0.015

in. were then taken. The shavings were finally sectioned into approximately 3/8" x 3/8" squares. The thin samples were deemed necessary in order to minimize end effects during reaction. The end result of this sample preparation technique was a collection of very flat, regular, reproducible samples of known dimensions.

As will be discussed later, the reaction process was determined to be reaction rate limited, not mass transfer limited as originally predicted. Therefore, as long as the wood chip size is kept below the size at which mass transfer becomes important (yet to be determined), the samples need not be prepared as carefully or uniformly as those used in these investigations.

Experimental Setup and Procedure

The experimental setup used in the gas phase HF saccharification experiments consists of four principal components: 1) HF source, 2) nitrogen source, 3) saccharification reactor, and 4) HF vapor exhaust motor. In addition to these main components, valves, meters, a temperature probe, and a heater are required. Figure 1 is a schematic of the reaction process.

With the boiling point of HF (19.5°C) fairly close to room temperature, it was at first believed that an adequate HF flow could be maintained at room temperature conditions without need of a heater. However, because the process of vaporization tends to cool the liquid fraction remaining in the tank, the HF flow continually diminished as the driving force for vaporization was reduced. After only a few minutes, the HF flow stopped. A heating block was then added to the HF source with metal spheres filling the gaps to aid in heat transfer. The portion of the tank not directly heated was covered with several layers of insulation to minimize heat losses. The HF tank, supplied by Matheson Gas Company, would not allow heating above 125°F for safety reasons, but 125°F was found to be quite

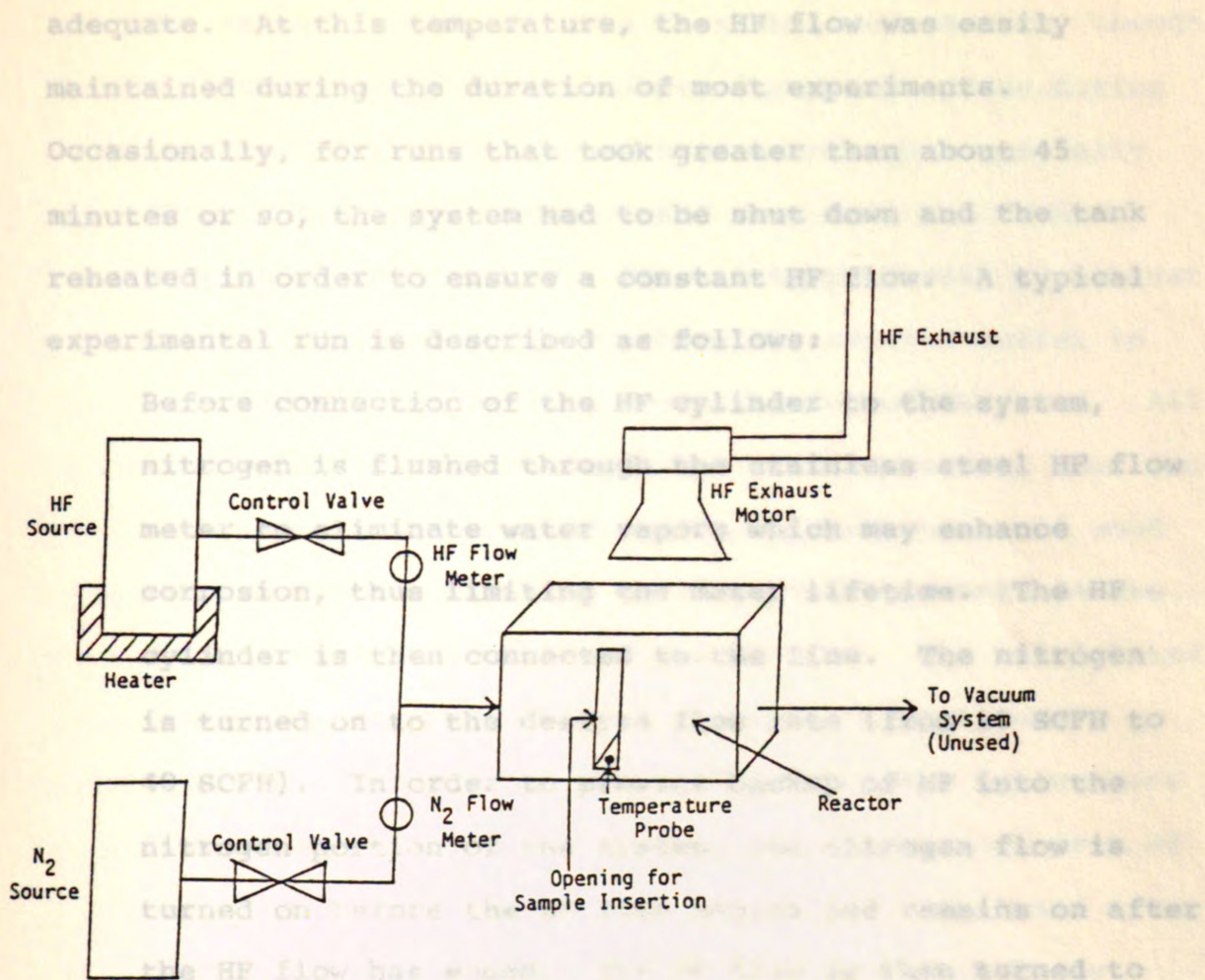


Figure 1. Gas Phase HF Saccharification Reaction System

with an HF flow rate of 10 SCFH. (The flow rate was maintained the minimum accurately possible with the existing HF flow meter.) As the HF flow rate was increased, the temperature drops due to the heat of mixing; the greater the percentage of HF, the greater the reduction in temperature. The temperature drop is most likely due to the heat of mixing of polymerization. The HF flow rate was then turned to nitrogen. Heat is then added to the system to dissociate the polymer.

adequate. At this temperature, the HF flow was easily though maintained during the duration of most experiments. during Occasionally, for runs that took greater than about 45 ally minutes or so, the system had to be shut down and the tank reheated in order to ensure a constant HF flow. A typical reactor outlet to experimental run is described as follows:

Before connection of the HF cylinder to the system, All nitrogen is flushed through the stainless steel HF flow meter to eliminate water vapors which may enhance wood corrosion, thus limiting the meter lifetime. The HF cylinder is then connected to the line. The nitrogen and is turned on to the desired flow rate (from 10 SCFH to 40 SCFH). In order to prevent backup of HF into the nitrogen portion of the system, the nitrogen flow is of turned on before the HF flow begins and remains on after the HF flow has ended. The HF flow is then turned to the desired level. (All studies performed were done ing with an HF flow rate of 6 SCFH which represented the minimum accurately measurable flow using the existing HF flow meter.) As the HF and nitrogen mix, the temperature drops due to the endothermic heat of mixing; the greater the percentage of nitrogen present, the greater the reduction in temperature. The temperature drop is most likely due to the reduction in the degree of polymerization of the HF upon mixing with the nitrogen. Heat is absorbed from the system to react dissociate the polymer, hence the drop in temperature.

The temperature is allowed to stabilize somewhat, though a fluctuation of several degrees may take place during the run. The HF/N₂ vapors travel through a specially constructed teflon reactor and then exit the front portion of the reactor. For safety purposes, an exhaust motor is mounted directly above the reactor outlet to draw the vapors upward and out the top of the hood. All studies using HF were performed inside a safety hood and with appropriate protection. Previously prepared wood samples, on the order of 0.015 g, are then held in the HF/N₂ flow for varying lengths of time. The initial and final temperatures for each individual sample are recorded. The samples are held in the flow by tweezers clamped at a corner of the sample. The surface area of the chip covered by the tweezers is very small and considered negligible for the purpose of this study. After reaction, samples are quenched in vials containing approximately 2 ml of water and a known amount of myo-inositol, used as an internal standard. The samples are then neutralized with calcium carbonate, centrifuged, and decanted. The solid fraction, containing lignin, ash, calcium carbonate, and other impurities, is discarded. The liquid fraction, containing soluble sugars, is kept for analysis. The HF flow is shut off, and the HF tank is disconnected. Finally, nitrogen is flushed through the HF flow meter to remove any traces of HF vapor. The entire

experimental procedure typically lasts from 3 to 5 hours. In order to prevent possible sugar degradation over time, the samples are kept frozen. Prior to subsequent derivatization and analysis, the desired samples are removed from cold storage and thawed.

After the reacted wood samples have been quenched, centrifuged, and decanted, the liquid fraction is thawed, cooled, and analyzed for sugar content. Because the sugars tend to form reversion oligomers, there will be an oligomeric distribution of these sugars present in the reaction mixture. HPLC was performed on the samples in order to get an idea of the reversion oligomeric distribution as the reaction progressed. Hewlett Packard 62A and 87P columns were employed for this analysis. The HPLC was used only qualitatively due to limitations of the system precluding the determination of exact yield data which were obtained using GC-MS for the purpose of analysis. The oligomeric sugars were hydrolyzed using a posthydrolysis using sulfuric acid to reduce the sugars to monomer. The monomers were then derivatized to glucose, xylose, and arabinose using a derivatization internal standard. The derivatized samples and the internal standard were then analyzed using GC-MS. The acetate derivatives were then analyzed using GC-MS for analysis. From the GC-MS data, the amounts of glucose and xylose were obtained.

Both the HPLC and GC apparatuses were coupled to an IBM-9000 computer system outfitted with a chromatography applications package. Each HPLC and GC run took on the order of 1 hour while Analysis Methods on procedure itself required approximately 8 hours.

After the reacted wood samples have been quenched, centrifuged, and decanted, the liquid fraction is thawed, cooled, and analyzed for sugar content. Because the sugars tend to form reversion oligomers, there will be an oligomeric distribution of these sugars present in the reaction mixture. HPLC was performed on the samples in order to get an idea of the trends in the oligomeric distribution as the reaction proceeds. Biorad Aminex 42A and 87P columns were connected in series for this analysis. The HPLC was used only qualitatively. Inherent limitations of the system precluded the calculation of actual yield data which were obtained through derivatization and GC analysis. The oligomeric sugar samples were subjected to a posthydrolysis using trifluoroacetic acid, thus reducing the sugars to monomer. The resulting solution contained glucose, xylose, and mannose, as well as the myo-inositol internal standard. The monomeric sugars and myo-inositol standard were then converted to their more volatile alditol acetate derivatives to facilitate gas chromatographic analysis. From the GC results, actual yields of glucose and xylose were obtained.

Both the HPLC and GC apparatuses were coupled to an IBM-9000 computer system outfitted with a chromatography applications package. Each HPLC and GC run took on the order of 1 hour while the derivatization procedure itself required approximately 8 hours.

The IBM 9000 computer coupled to a gas chromatograph determined the number of moles of xylose or glucose relative to the number of moles of myo-inositol internal standard. Since the amount of internal standard present was precisely known, the moles of sugar were determined. To derive yield data, the theoretical amount of sugar present in the Bigtooth Aspen raw wood had to be known. These values are 3.441×10^{-3} moles glucose/g wood and 1.4×10^{-3} moles xylose/g wood (4). Tables 3-7 represent the laboratory yield data obtained at five specified flow conditions. The yields are listed as a fraction of theoretical yield. In several of the runs, a point or two is rather inconsistent with the majority of the rest of the data. These points have asterisks (*) beside them in the tables.

Each experimental run was analyzed using the KINFIT computer program developed at Michigan State University (19). This program determined the best fit of the proposed first-order reaction model to the experimental data. Figures 2-6 give the sugar yield data and the computer-determined best first-order fit. (The glucose yields were about zero for the two low 100°C conditions.) Initially, the temperatures were varied with

TABLE 3
Sugar Yields for a Flow of 6 SCFH HF/0 SCFH N₂

Sample	Time (Sec)	Average Yield		Average Temp (°C)
		Xylose	Glucose	

Yields, Kinetics, and HPLC Results (Simplified Model)

1	7	0.557	0.000	26.03
2	11	0.696	0.033	26.40
3	20	0.814	0.133	26.15
4	30	0.725	0.260	25.65
6	40	0.826	0.374	24.45
8	70	1.078	*0.877	24.40
10	100	0.947	0.933	26.10
12	120	*0.750	0.833	25.70

The IBM 9000 computer coupled to a gas chromatograph determined the number of moles of xylose or glucose relative to the number of moles of myo-inositol internal standard. Since the amount of internal standard present was precisely known, the moles of sugar were determined. To derive yield data, the theoretical amount of sugar present in the Bigtooth Aspen raw wood had to be known. These values are 3.441×10^{-3} moles glucose/g wood and 1.4×10^{-3} moles xylose/g wood (4). Tables 3-7 represent the laboratory yield data obtained at five specified flow conditions. The yields are listed as a fraction of theoretical yield. In several of the runs, a point or two is rather inconsistent with the majority of the rest of the data. These points have asterisks (*) beside them in the tables.

Each experimental run was analyzed using the KINFIT computer program developed at Michigan State University (19). This program determined the best fit of the proposed first-order reaction model to the experimental data. Figures 2-6 give the sugar yield data and the computer-determined best first-order fit. (The glucose yields were about zero for the two most dilute HF conditions.) Initially, the temperatures were included with

TABLE 3
 Sugar Yields for a Flow of 6 SCFH HF/O/SCFH N₂

Sample	Time (Sec)	Average Yield		Average Temp (°C)
		<u>Xylose</u>	<u>Glucose</u>	
1	17	0.557	0.000	26.05
2	11	0.696	0.033	26.40
3	15	0.681	0.063	25.35
4	20	0.814	0.133	26.15
5	25	0.903	0.168	26.00
6	30	0.725	0.260	25.65
7	35	0.842	0.337	25.30
8	40	0.826	0.374	24.45
9	52	0.957	0.455	24.80
10	70	1.078	*0.877	24.40
11	80	0.842	0.667	26.40
12	100	0.947	0.803	26.10
13	100	*0.788	0.672	26.10
14	120	*0.750	0.642	25.70
15	180	0.981	0.749	25.50

TABLE 4
Sugar Yields for a Flow of 6 SCFH HF/10 SCFH N₂

Sample	Time (Sec)	Average Yield		Average Temp (°C)
		<u>Xylose</u>	<u>Glucose</u>	
1	10	0.468	0.000	21.15
2	20	0.605	0.009	20.40
3	40	0.713	0.061	20.55
4	70	0.677	0.236	20.45
5	100	0.781	0.426	20.35
6	140	0.796	0.560	20.70
7	180	0.955	0.719	21.30
8	210	*0.728	0.736	21.65

TABLE 5
Sugar Yields for a Flow of 6 SCFH HF/20 SCFH N₂

Sample	Time (Sec)	Average Yield <u>Xylose</u>	Average Yield <u>Glucose</u>	Average Temp (°C)
1	10	0.081	0.000	12.95
2	20	0.355	0.000	12.50
3	40	0.530	0.000	12.25
4	70	0.795	0.000	11.75
5	100	0.644	0.014	11.35
6	140	*0.535	0.025	11.05
7	180	0.990	0.060	10.65
8	240	0.946	0.077	10.65
9	300	0.828	0.081	9.40

TABLE 6
Sugar Yields for a Flow of 6 SCFH HF/30 SCFH N₂

Sample	Time (Sec)	Average <u>Xylose</u>	Yield <u>Glucose</u>	Average Temp (°C)
1	10	0.056	0.000	10.25
2	20	0.196	0.000	9.60
3	30	0.391	0.000	9.05
4	40	0.478	0.000	8.40
5	50	0.651	0.000	8.40
6	70	0.987	0.000	8.35
7	90	0.952	0.000	7.95
8	120	0.786	0.000	7.40
9	180	0.748	0.000	7.40
10	360	---	0.025	7.90
11	600	---	0.032	5.05

TABLE 7
Sugar Yields for a Flow of 6 SCFH HF/40 SCFH N₂

Sample	Time (Sec)	Average <u>Xylose</u>	Yield <u>Glucose</u>	Average Temp (°C)
1	10	---	0.000	6.15
2	30	0.202	0.000	5.50
3	52	0.578	0.000	5.05
4	73	*0.807	0.000	4.25
5	90	0.619	0.000	3.30
6	120	0.691	0.000	2.75
7	160	*0.491	0.000	1.85
8	220	0.927	0.000	1.65
9	325	1.033	0.000	1.20
10	480	---	0.020	2.20
11	900	---	0.024	2.85

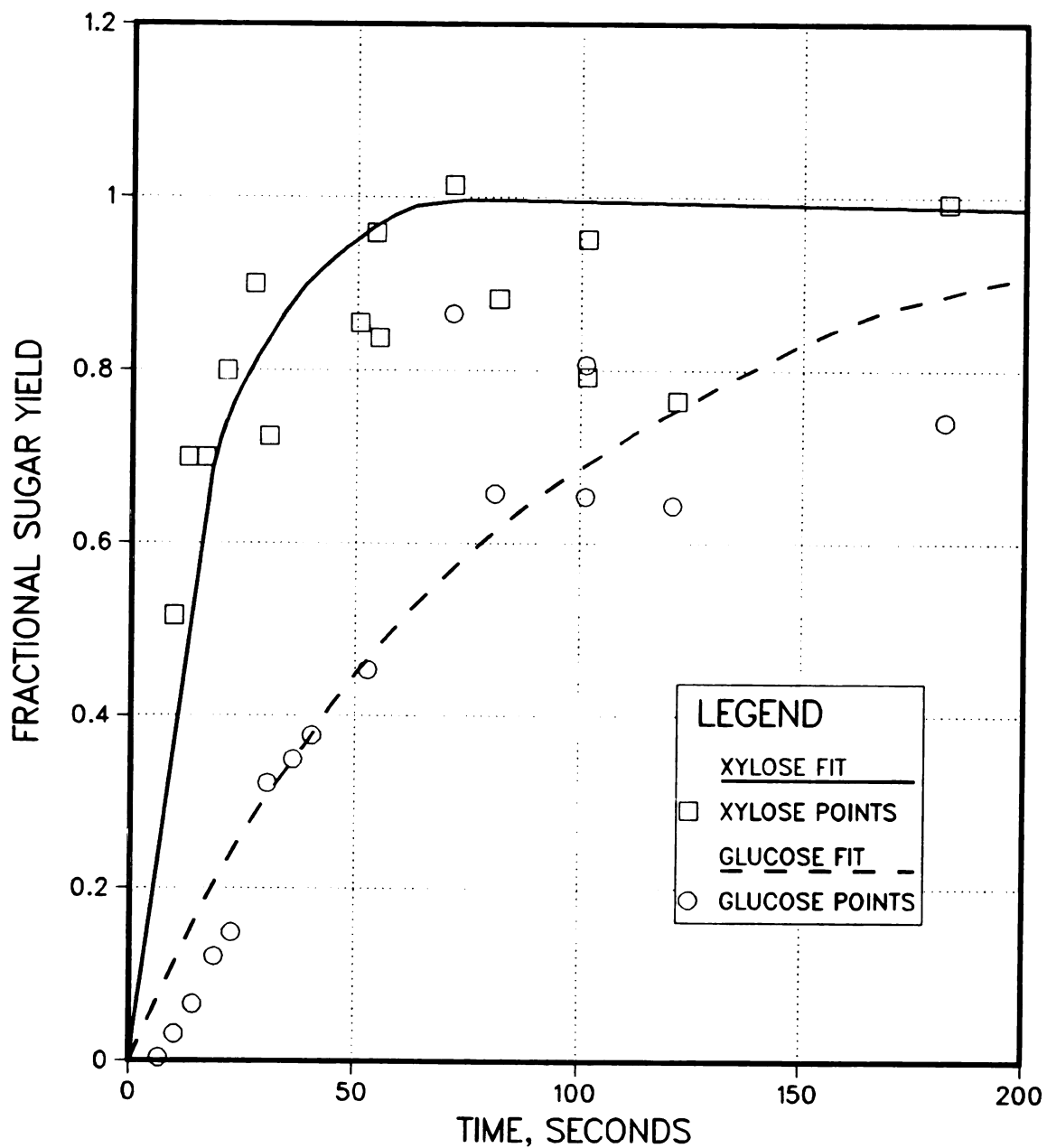


Figure 2. Sugar Yields for Conditions of 6 SCFH HF/0 SCFH N_2 (AVG T = 25.7°C)

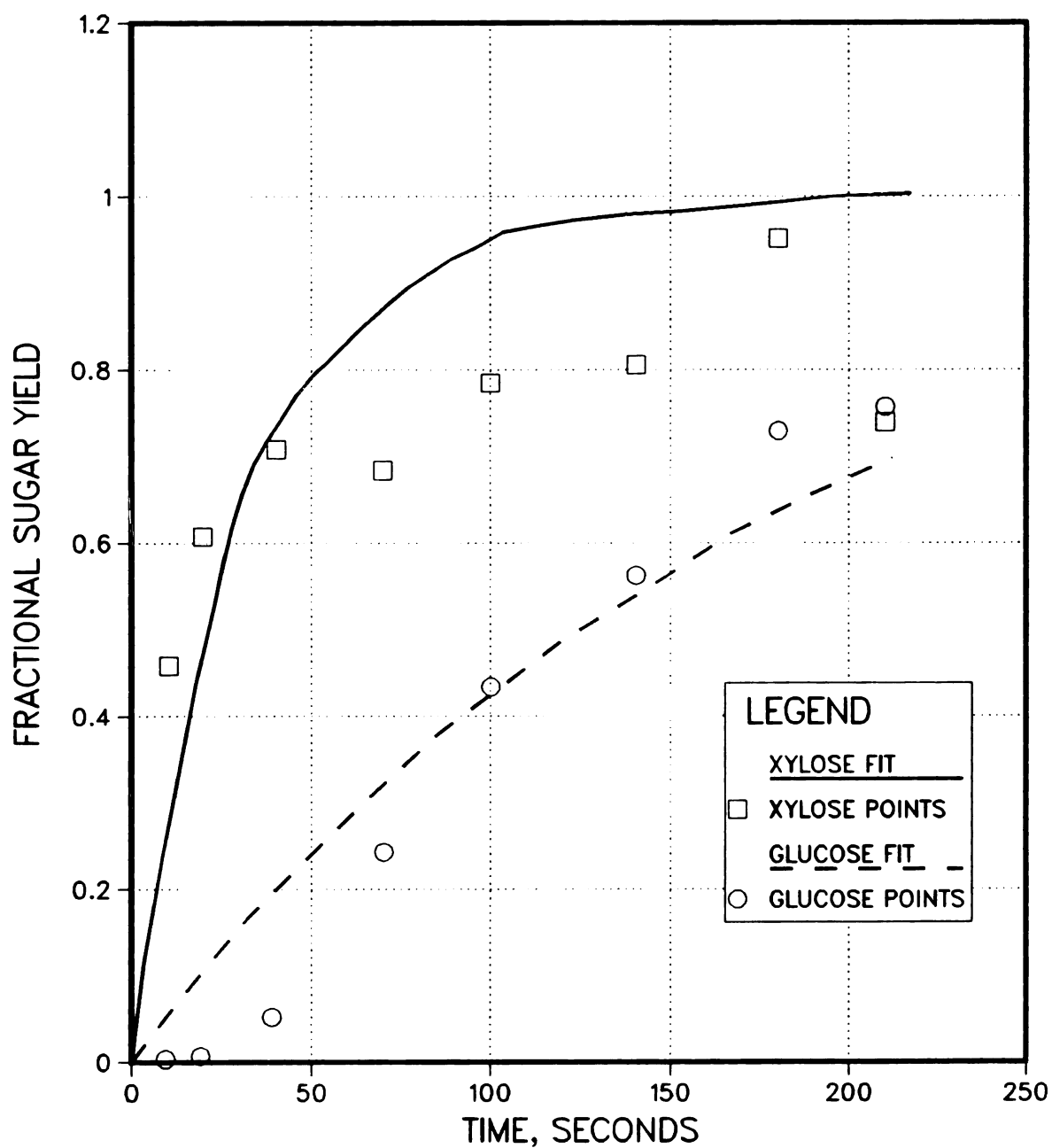


Figure 3. Sugar Yields for Conditions of 6 SCFH HF/10 SCFH N_2 (AVG T = 20.8°C)

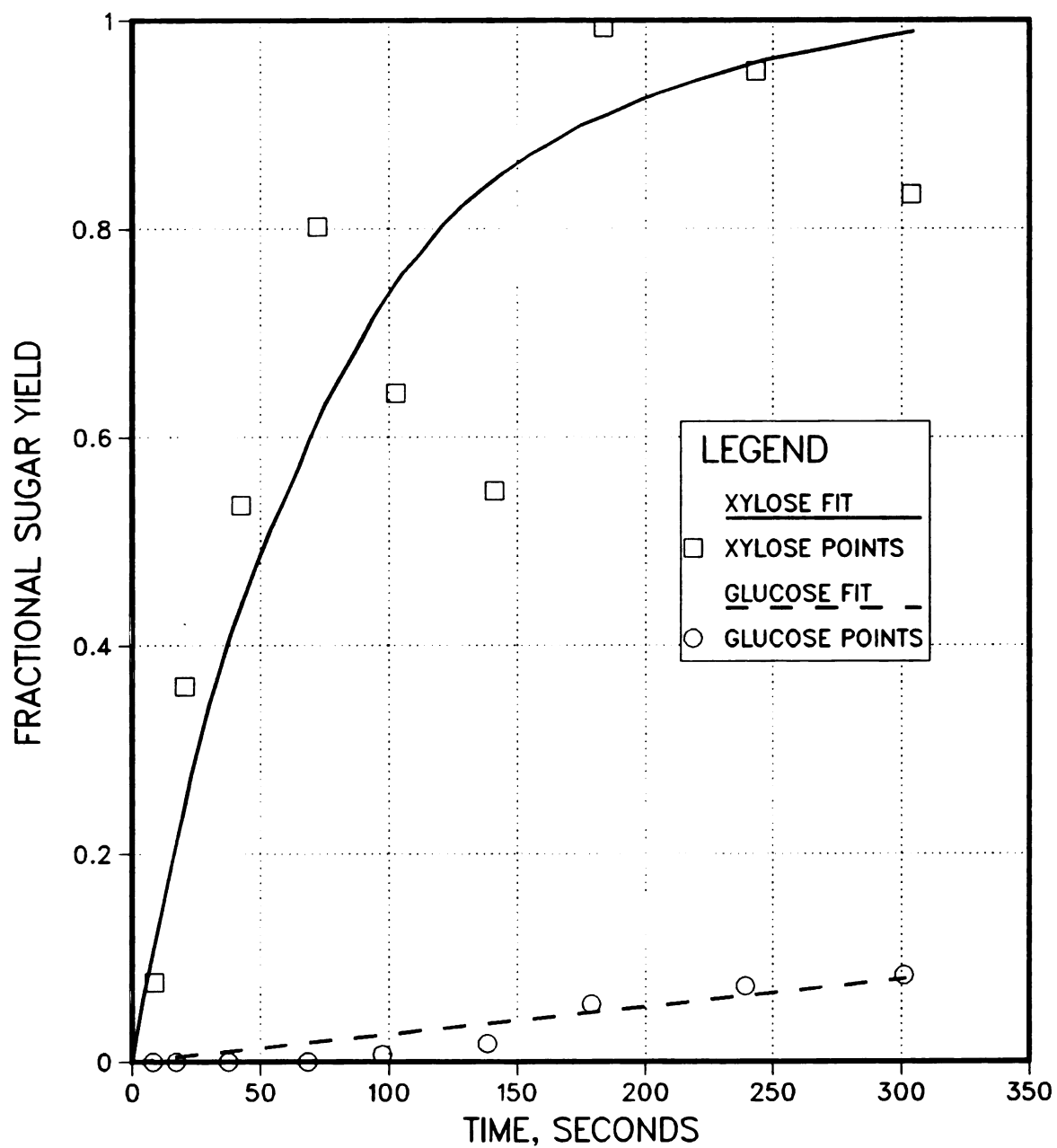


Figure 4. Sugar Yields for Conditions of 6 SCFH HF/20 SCFH N_2 (AVG $T = 11.4^{\circ}C$)

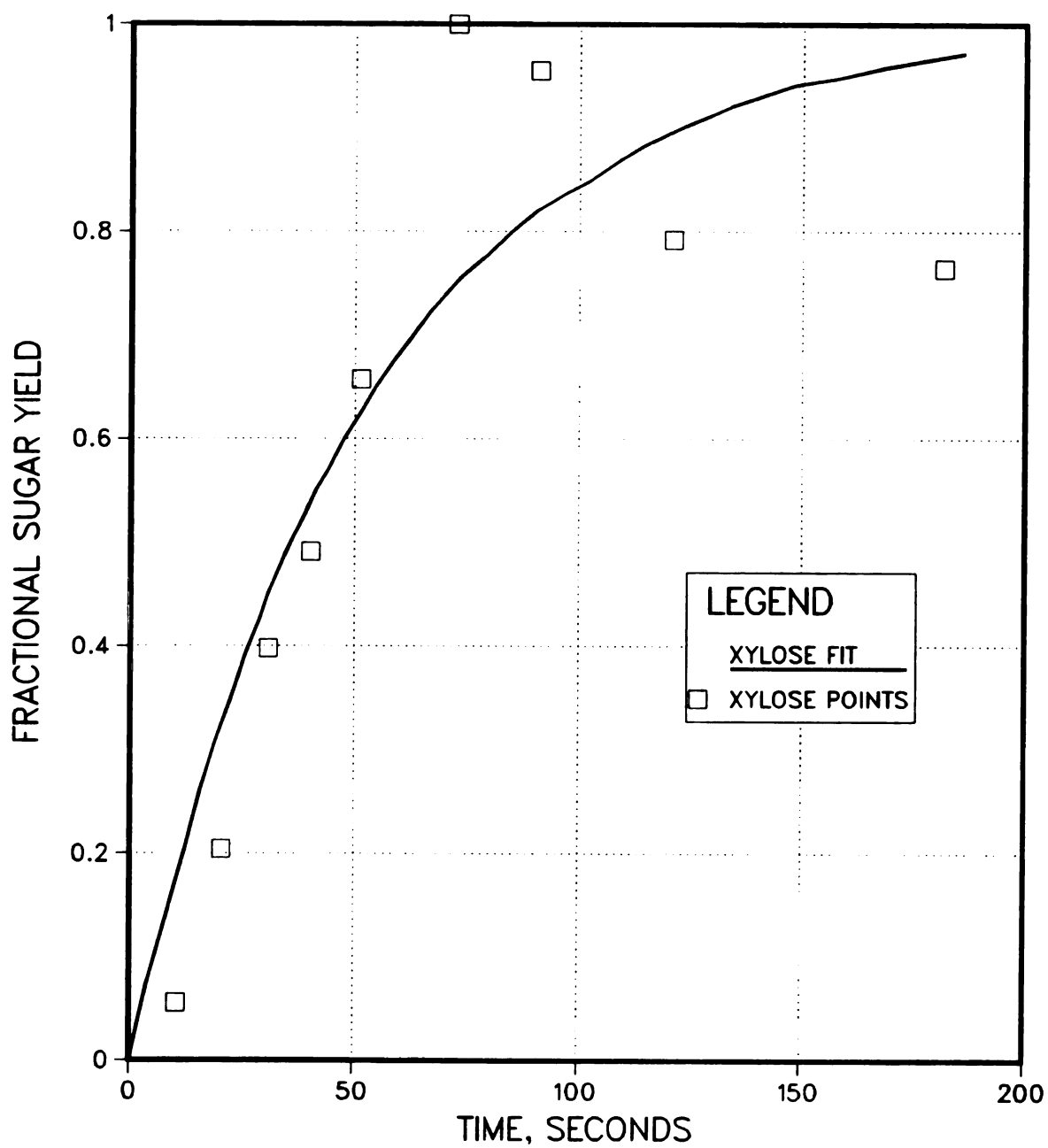


Figure 5. Sugar Yields for Conditions of 6 SCFH HF/30 SCFH N_2 (AVG T = 8.5°C)

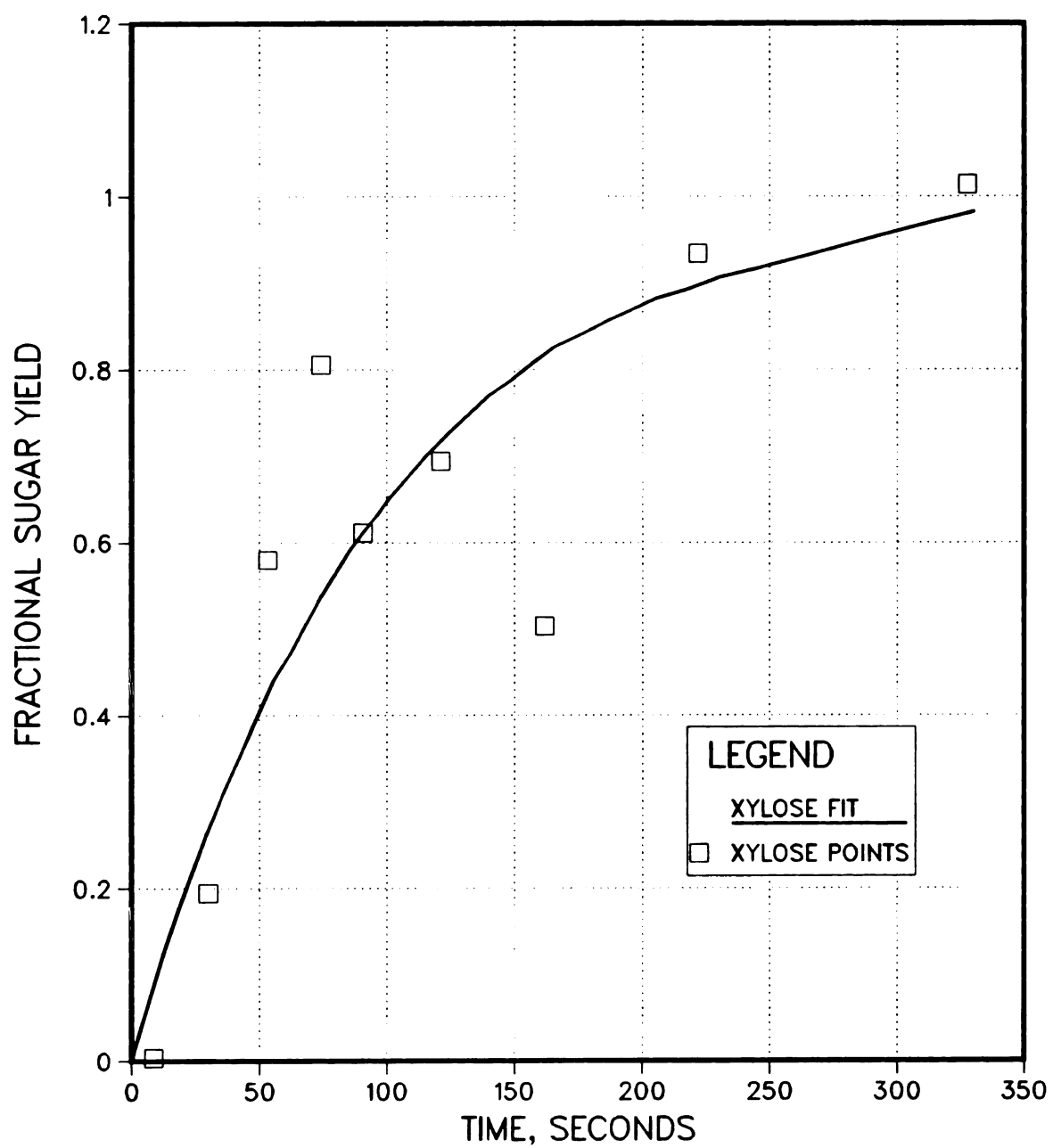


Figure 6. Sugar Yields for Conditions of 6 SCFH HF/40 SCFH N_2 (AVG $T = 3.5^{\circ}C$)

the time and yield data in an attempt to determine rate constants and activation energies for each individual run. However, because of mathematical instabilities caused by a range of data insufficient for a two parameter fit, the results were unsatisfactory. The five runs were then lumped together to determine one overall rate constant (at 20°C) and one activation energy for glucose and for xylose. Table 8 contains the results of this analysis. Since the computer results of each individual run were less than desirable, the validity of the overall rate constants and activation energies were questionable without further corroboration. For that reason, a second analysis was performed using KINFIT. In this analysis, an average temperature was used for each run. A rate constant was determined from the best fit of the first order model to the experimental data. Tables 9 and 10 contain this data.

Rate constants were determined for each run, first using all of the data points and second using only the best data points, i.e., excluding those points with asterisks, see Tables 3-7. As evident from Tables 9 and 10, including even the questionable points did not significantly alter the derived rate constant values, at least at the higher temperatures. Using the average temperature and rate constant values (using all data points) an Arrhenius plot was made for both glucose and xylose. (See Figures 7 and 8.) From the slope of this plot, activation energies for each sugar were determined. The obtained activation

TABLE 8
Rate Constants and Activation Energies
(Using All Data Points at the Experimental Temperatures)

	<u>Xylose</u>	<u>Glucose</u>
K(sec ⁻¹)	4.36 x 10 ⁻²	3.86 x 10 ⁻³
K St. Dev.	5.07 x 10 ⁻³	3.27 x 10 ⁻⁴
Ea (Cal/gmole)	1.42 x 10 ⁴	3.62 x 10 ⁴
Ea St. Dev.	1.69 x 10 ³	2.83 x 10 ³

TABLE 9
Glucose Rate Constants

Flow (SCFH HF/SCFH N ₂)		Average Temp. (°C)	K (sec ⁻¹)	St. Dev.
6/0	All Points	25.66	1.20×10^{-2}	1.27×10^{-3}
6/0	Best "	25.66	1.07×10^{-2}	8.20×10^{-4}
6/10	All "	20.82	5.52×10^{-3}	5.93×10^{-4}
6/20	All "	11.39	2.78×10^{-4}	2.77×10^{-5}
6/30	All "	8.53	5.14×10^{-5}	6.43×10^{-6}
6/40	All "	3.52	2.51×10^{-5}	4.06×10^{-6}

TABLE 10
Xylose Rate Constants

Flow (SCFH HF/SCFH N ₂)		Average Temp. (°C)	K (sec ⁻¹)	St. Dev.
6/0	All Points	25.66	8.22 x 10 ⁻²	1.35 x 10 ⁻²
6/0	Best "	25.66	8.22 x 10 ⁻²	1.07 x 10 ⁻²
6/10	All "	20.82	3.18 x 10 ⁻²	9.81 x 10 ⁻³
6/10	Best "	20.82	3.22 x 10 ⁻²	9.02 x 10 ⁻³
6/20	All "	11.39	1.36 x 10 ⁻²	2.89 x 10 ⁻³
6/20	Best "	11.39	1.69 x 10 ⁻²	2.72 x 10 ⁻³
6/30	All "	8.53	1.92 x 10 ⁻²	3.32 x 10 ⁻³
6/40	All "	3.52	1.06 x 10 ⁻²	2.33 x 10 ⁻³
6/40	Best "	3.52	1.29 x 10 ⁻²	1.91 x 10 ⁻³

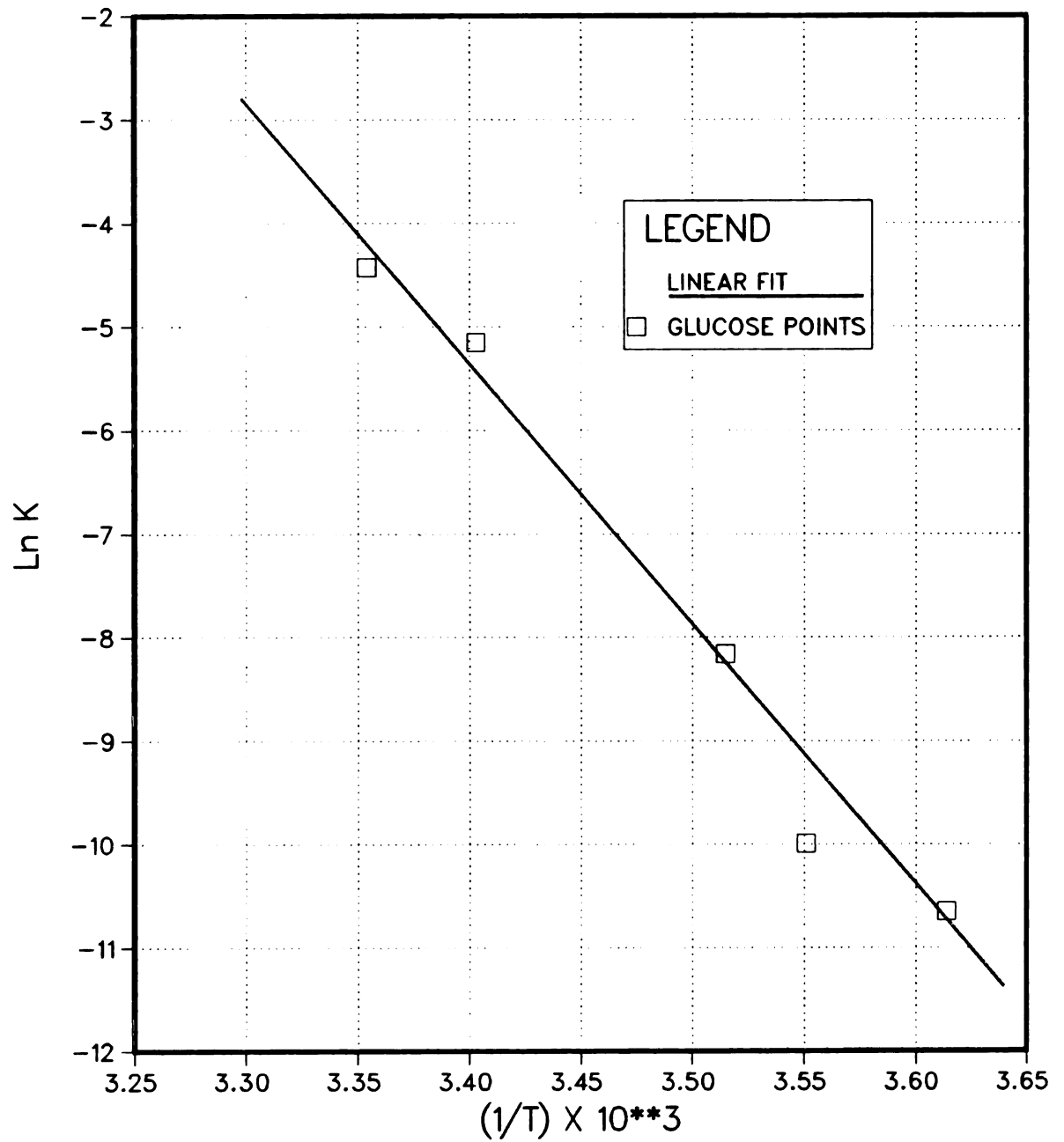


Figure 7. Glucose Arrhenius Plot for Activation Energy Determination

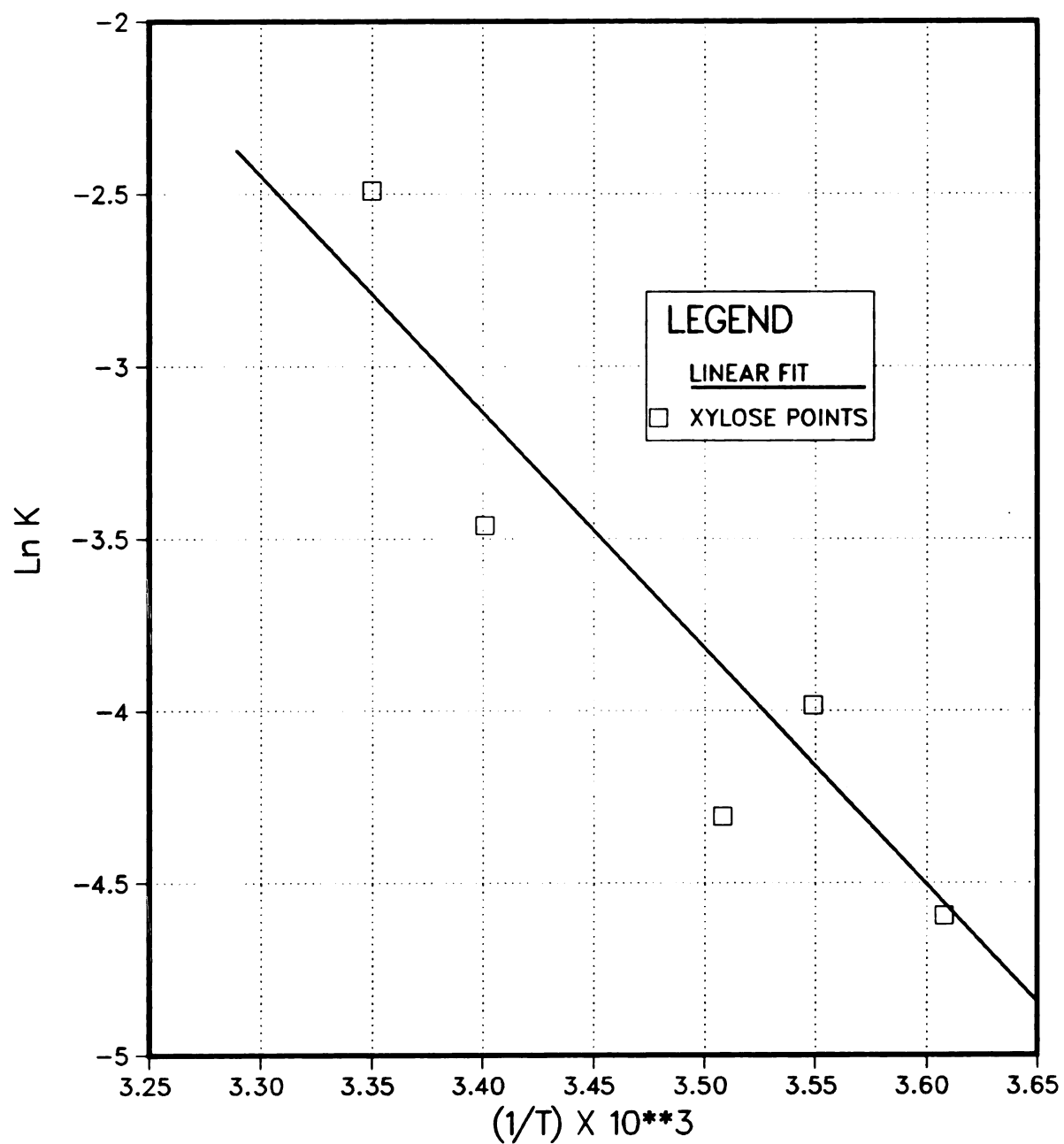


Figure 8. Xylose Arrhenius Plot for Activation Energy Determination

energies as well as the rate constants at 20°C were compared to those values derived in the initial computer analysis which included different temperatures for each point. Though the values differ somewhat, they are sufficiently close to lend credence to both the first-order model simulation as well as the computer analysis procedure.

In addition to GC analyses which provided yield data, HPLC analyses were performed for each sample of each run. The resulting chromatographs were analyzed to determine trends in the oligomeric distribution of the reaction mixtures. Figures 9 and 10 show representative HPLC chromatographs at the specified conditions. The actual analysis of the HPLC results is contained in the Discussion portion of this paper.

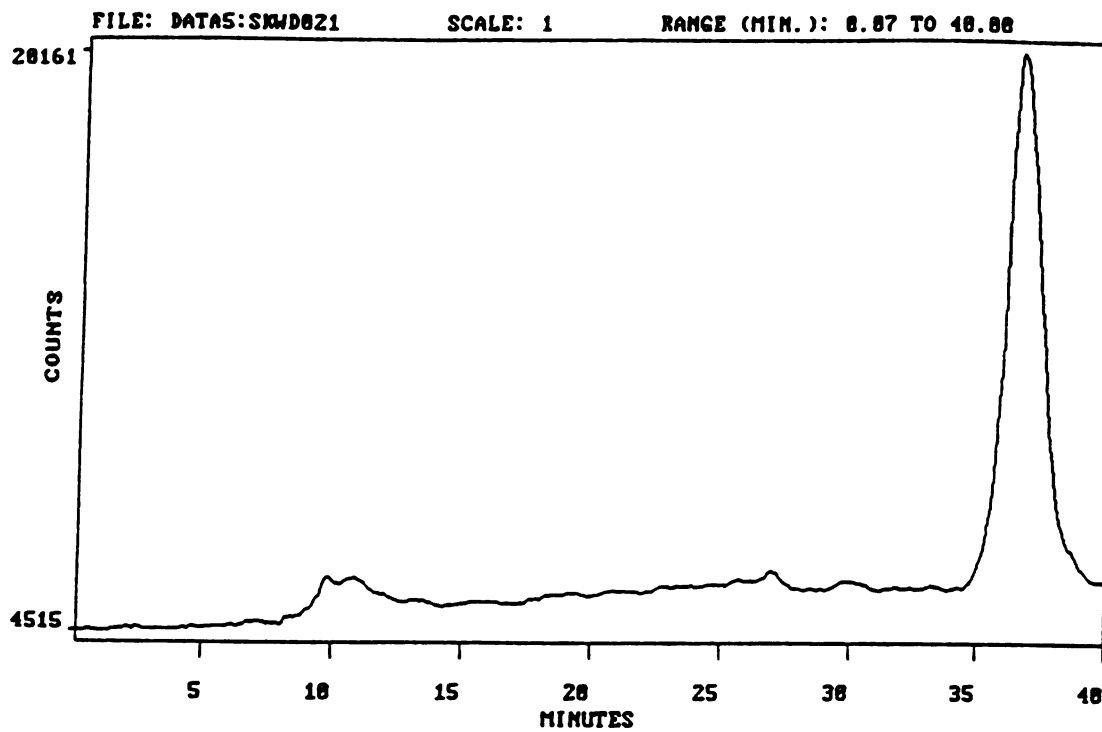


Figure 9. HPLC Chromatogram for Conditions of 6 SCFH HF/0
SCFH N₂ Reacted for 5 Seconds

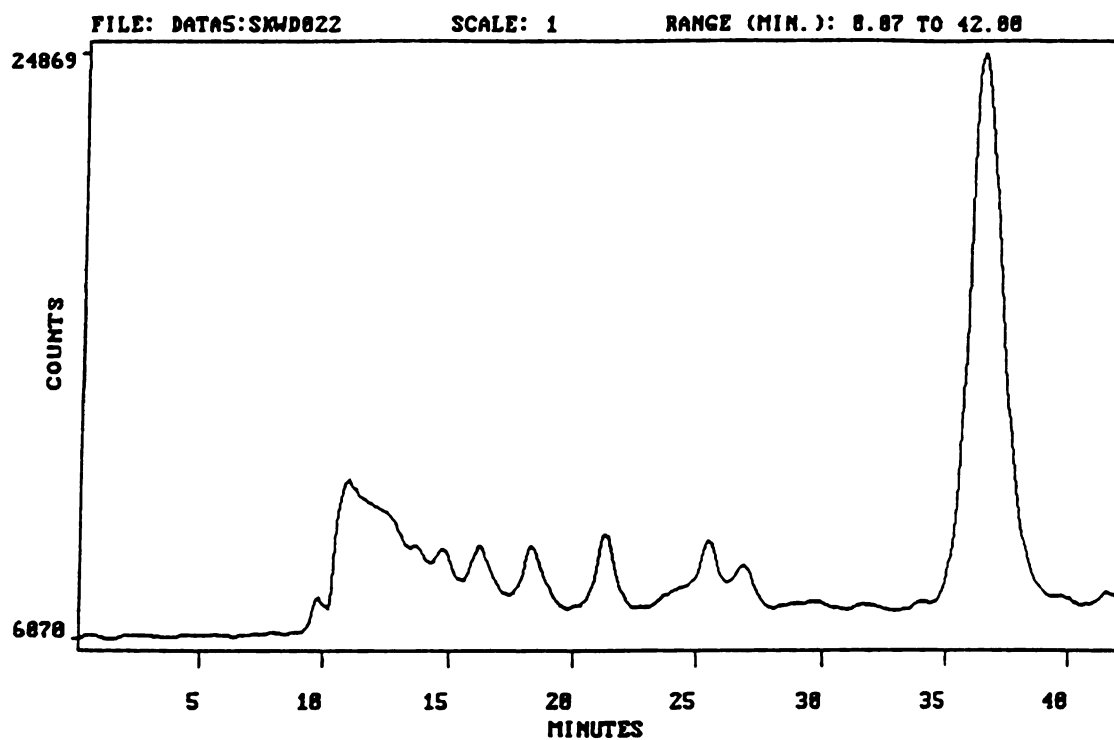
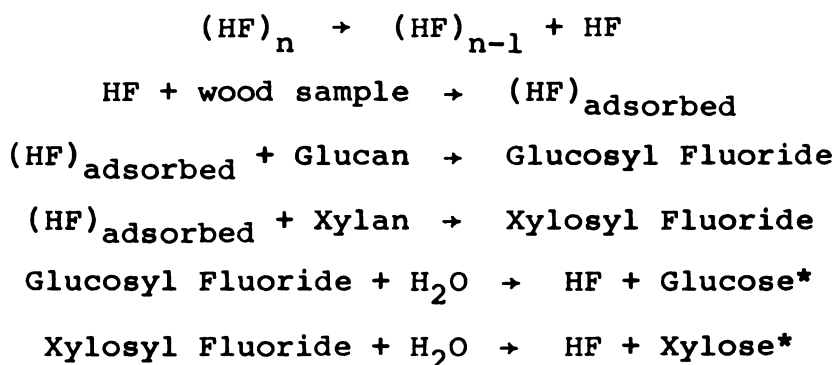


Figure 10. HPLC Chromatogram for Conditions of 6 SCFH HF/0
SCFH N₂ Reacted for 70 Seconds

POSSIBLE HF PARTIAL PRESSURE DEPENDENCE

The reaction of hydrogen fluoride with wood is represented by the following mechanism:



*(monomer or reduced polymer)

The adsorbed HF is most likely present in monomer form, either adsorbed directly from the gas stream or produced as part of an HF polymer dissociation at the wood surface. The adsorbed HF reacts with the glucan and xylan fractions of the wood sample producing the corresponding sugar fluorides. Addition of water regenerates the HF and produces glucose and xylose, either in monomeric or reduced-DP polymer form.

The reaction model presented in section VI of this work essentially neglects the effects of HF concentration. This omission was deemed permissible for two reasons: 1) The

HF/wood reaction can be viewed as a degradation reaction which are generally first order. Thus, the rate could be viewed as a function of sugar concentration only. 2) The assumption allowed a relatively quick way to arrive at ballpark rate constants and activation energies. However, since it is unlikely that the HF/wood reaction is totally independent of HF partial pressure, it was desired to investigate the approximate magnitude of this dependence. The general procedure followed (20) was to arrange each rate constant expression in Arrhenius form at a constant reference reaction temperature. By choosing a comparable reaction time, a sugar yield scaled to the same conditions could be calculated for each of the five HF/N₂ ratios investigated. Plots of glucose and xylose yield versus HF partial pressure could then be made. This procedure required one important assumption: that the activation energy and reference temperature rate constant (k_0) have a negligible dependence on the HF concentration. Therefore, the activation energies and rate constants calculated assuming the previous simplified model could be used (see Tables 8, 9, and 10).

Taking the previous model result for glucose

$$C_c = C_{c_0} e^{-kt}, \quad \frac{C_c}{C_{c_0}} = e^{-kt}$$

and the Arrhenius form of the rate constant, one obtains the following expression:

$$Y_g = 1 - \exp \left\{ k_o \exp \left[- \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] t \right\}$$

where $Y_g \equiv 1 - e^{-kt}$ and the other variables are defined as before. A similar expression (Y_x) can be written for xylose. We now assume a reference reaction time of 200 seconds, a reference reaction temperature (T_o) of 298.15°K, and define the HF partial pressure as

$$P_{HF} = \frac{F_{HF}}{F_{HF} + F_{N_2}} P_T$$

where P_{HF} = HF partial pressure

F_{HF} = HF flow in SCFH

F_{N_2} = N_2 flow in SCFH

P_T = total pressure (1 atm)

One can then set up expressions for the rate constant and in turn calculate the scaled sugar yields. Tables 11 and 12 give the rate constant expressions as a function of the reference reaction temperature for glucose and xylose, respectively. Tables 13 and 14 give the data pertinent to the calculation of the scaled sugar yields (Y_g and Y_x), and Figures 11 and 12 show the plots of scaled sugar yields versus HF partial pressure for glucose and xylose.

TABLE 11
Glucose Arrhenius-Form Rate Constant Expressions

<u>Flow (SCFH HF/SCFH N₂)</u>	<u>k Expression (sec⁻¹)*</u>
6/0	$k=1.07 \times 10^{-2} \exp \left[-\frac{18,217}{T_O} + 60.964 \right]$
6/10	$k=5.52 \times 10^{-3} \exp \left[-\frac{18,217}{T_O} + 61.968 \right]$
6/20	$k=2.78 \times 10^{-4} \exp \left[-\frac{18,217}{T_O} + 64.021 \right]$
6/30	$k=5.14 \times 10^{-5} \exp \left[-\frac{18,217}{T_O} + 64.671 \right]$
6/40	$k=2.51 \times 10^{-5} \exp \left[-\frac{18,217}{T_O} + 65.842 \right]$

* k_O taken from Table 9, best points.

E_a taken from Table 8.

$T_O = 298.15^\circ\text{K}$

TABLE 12
Xylose Arrhenius-Form Rate Constant Expressions

<u>Flow (SCFH HF/SCFH N₂)</u>	<u>k Expression (sec⁻¹)*</u>
6/0	$k=8.22 \times 10^{-2} \exp \left[-\frac{7146}{T_O} + 23.914 \right]$
6/10	$k=3.22 \times 10^{-2} \exp \left[-\frac{7146}{T_O} + 24.308 \right]$
6/20	$k=1.69 \times 10^{-2} \exp \left[-\frac{7146}{T_O} + 25.113 \right]$
6/30	$k=1.92 \times 10^{-2} \exp \left[-\frac{7146}{T_O} + 25.368 \right]$
6/40	$k=1.29 \times 10^{-2} \exp \left[-\frac{7146}{T_O} + 25.828 \right]$

*k_O taken from Table 10, best points.

E_a taken from Table 8.

T_O = 298.15°K

TABLE 13
Parameters for Scaled Glucose Yield Calculation

Flow (SCFH HF/SCFH N ₂)	P _{HF} (atm)	Reaction Temp(°K)	k(sec ⁻¹)	Y _g *
6/0	1.0	298.81	9.338x10 ⁻³	0.846
6/10	0.375	293.97	1.315x10 ⁻²	0.928
6/20	0.231	284.54	5.159x10 ⁻³	0.644
6/30	0.167	281.68	1.827x10 ⁻³	0.306
6/40	0.130	276.67	2.878x10 ⁻³	0.438

*Assumes: t = 200 seconds

$$T_o = 298.15^\circ\text{K}$$

TABLE 14
Parameters for Scaled Xylose Yield Calculation

Flow (SCFH HF/SCFH N ₂)	P _{HF} (atm)	Reaction Temp(°K)	k(sec ⁻¹)	Y _x *
6/0	1.0	298.81	7.789x10 ⁻²	1.0000
6/10	0.375	293.97	4.525x10 ⁻²	0.9999
6/20	0.231	284.54	5.312x10 ⁻²	1.0000
6/30	0.167	281.68	7.788x10 ⁻²	1.0000
6/40	0.130	276.67	8.288x10 ⁻²	1.0000

*Assumes: t = 200 seconds

$$T_o = 298.15^\circ\text{K}$$

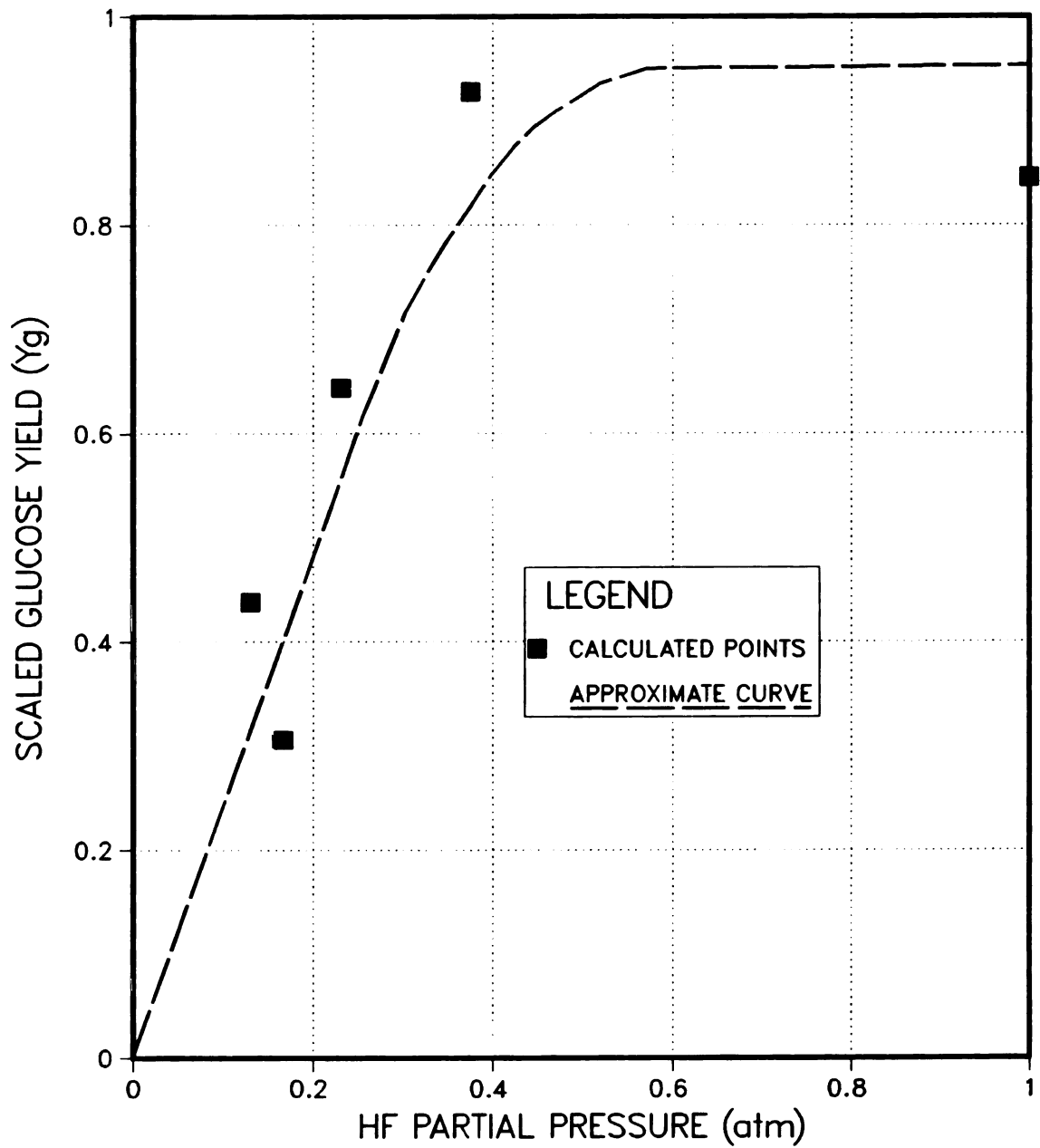


Figure 11. Scaled Glucose Yield as a Function of HF Partial Pressure

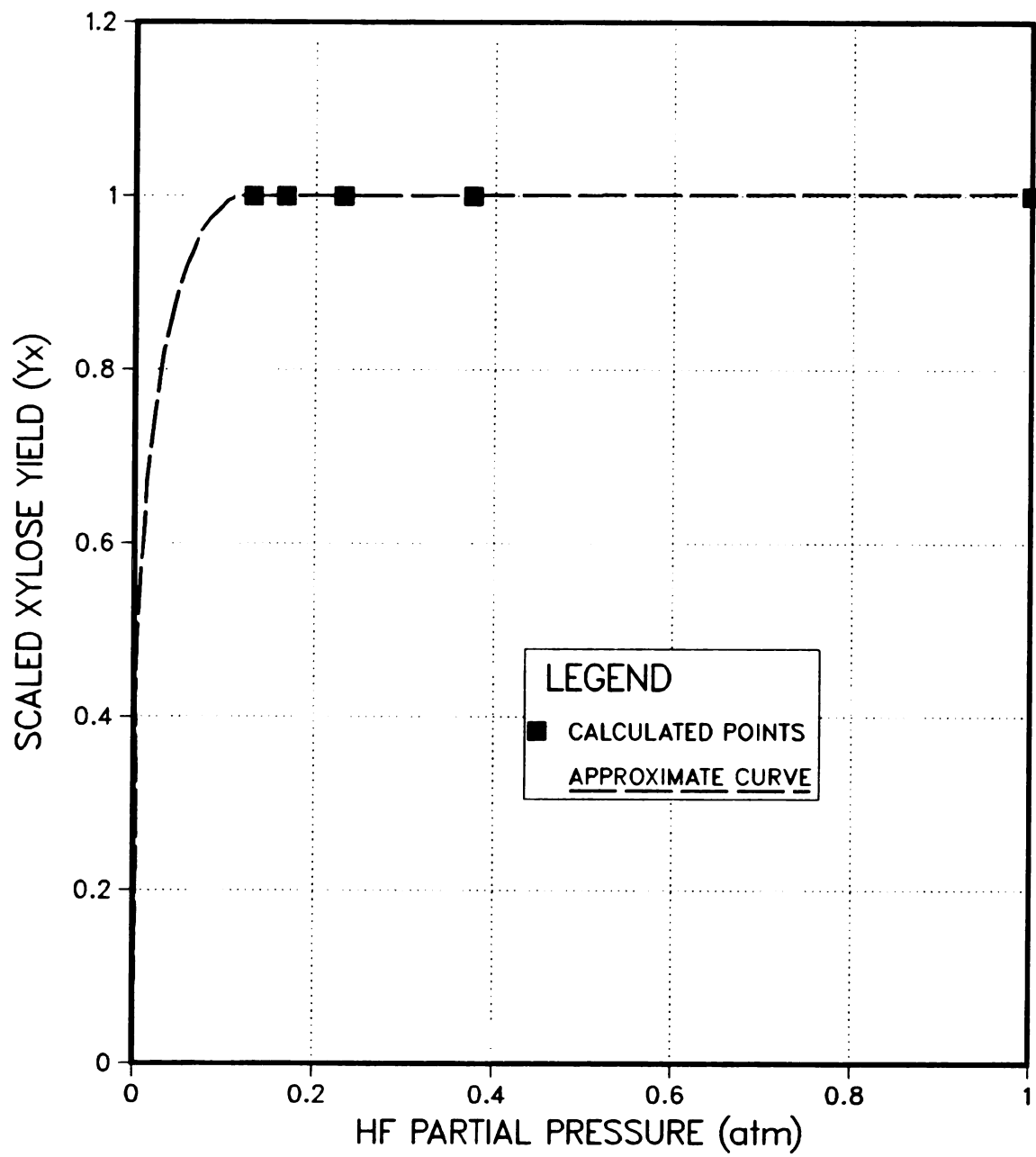


Figure 12. Scaled Xylose Yield as a Function of HF Partial Pressure

DISCUSSION

Once the flows have been established through the reactor, the chip/sample has been inserted, and the reaction has begun, the sample structure undergoes an interesting change. The normal wood color almost immediately changes to a very dark brown, but the rigid chip structure is maintained. However, as the reaction progresses, the structural integrity of the sample begins to degrade, and the chip becomes quite limp. Longer reaction times cause the disintegration to continue until the chip "flutters" in the gas flow. The structural degradation is due to the breakdown of the cellulose during reaction. As the cellulose breaks down, the lignin matrix begins to take on more of the structural burden. Finally, when the cellulose has completely reacted, the lignin network is the sole component tending to maintain some semblance of structure. At very long reaction times, at least at the highest temperature studied, the sample agglomerates into a teardrop shaped mass, i.e., the chip has completely broken down. These long-time samples were often times quite difficult to keep on the sample holders, and upon quenching in water, the resulting liquid was light brown in color signifying a near complete structural breakdown. The shorter-time samples

maintained most of their shape and left a relatively clear liquid upon quenching.

In general, from Figures 2-6 we can see that the conversion of xylan to xylose and glucan to glucose appears to be quite well approximated by the first-order fit determined by the KINFIT computer program. (This may have been somewhat fortuitous, at least for glucose, for reasons to be discussed later.) Several points though appeared to deviate inordinately from the first-order plot. There are several possible explanations for this, including: 1) Small portions of the chip may have been lost during reaction. The high temperature, long-time samples were quite "liquid like" and small portions could have easily been lost. 2) There may have been less (or more) glucan and/or xylan present in the particular unreacted sample used than is supposedly present in the raw wood sample. The values of 3.441×10^{-3} moles glucan/g wood and 1.4×10^{-3} moles xylan/g wood are average values for the standard tree, but depending on the particular portion of the tree used, the values may vary somewhat. The fact that the wood samples used, about 0.015 g per reaction sample, are quite small adds to the possibility that the actual "theoretical yield" will vary from one sample to the next. 3) For some of the runs, the reaction time between samples may not have been great enough to overcome the lowered reaction rate caused by a drop in temperature. 4) The structural shape of the sample (coalescence) may have hindered the reaction with HF.

During reaction, the sample would occasionally "fold up," thus lessening the area exposed to the HF and reducing yields. The added thickness may have been sufficient to allow the onset of mass transfer limitations. If no mass transfer limitations were present for any size sample, then of course the change in structural shape during reaction could not be an explanation for possible error.

Initially, it was thought that the different HF/N₂ ratios would have no affect on yields other than by merely changing the operating temperature. This was found to be probable for xylose but not for glucose. The Arrhenius plots of Figures 7 and 8 generally follow what would be expected of a reaction system where only the temperature is changed. The plots appear quite linear for xylose and especially linear for glucose. Therefore, the assumption that the change of HF/N₂ relative flows was to only change the operating temperature appeared plausible. The exercise of Section VIII in which the approximate sugar yield dependence on HF partial pressure was determined, however, tended to dispute the assertion for glucose but reinforce it for xylose. Figure 11 shows that glucose yield is indeed a function of HF concentration. Figure 12, on the other hand, shows that the original omission of HF concentration in the reaction model was probably reasonable for xylose, at least for the assumed 200-second reference reaction time. At even the most dilute HF concentration, the scaled xylose yield was virtually quantitative. For reaction times of 200

seconds or longer, therefore, the xylose conversion is essentially independent of HF partial pressure. The general conclusion is then that the proposed simple model is acceptable for xylose but that a more complex model incorporating HF concentration is required for glucose. The comprehensive glucose model will probably be of the form

$$r = k C_{\text{HF}}^a C_g^b$$

where r = the reaction rate

k = the rate constant

C_{HF} = HF concentration

C_g = glucan concentration (or xylan)

a, b = constants.

Only further research will determine if the above proposed form is correct.

The rate constants and activation energies obtained from the computer analysis differ markedly from the values given by Selke for liquid phase HF reaction (4). Since only anhydrous conditions were investigated in this work, the only readily comparable values from the liquid phase studies are those obtained for similarly anhydrous conditions. Selke lists the value of 0.179 min^{-1} and $12,490 \text{ cal/gmole}$ as the rate constant (3.9°C) and activation energy respectively for glucose (4). The closest temperature studied for the gas phase is 3.5°C , corresponding to the 6 SCFH HF/40 SCFH N_2 flow conditions, and the calculated rate constant value is on the order of 0.0015 min^{-1} . The value is very much

lower than that for the liquid phase. Accepting these at face value, the conclusion is that at least for glucose the liquid phase reaction is superior to gas phase operation at 3.5 - 4.0°C. The glucose activation energy for the gas phase system is calculated to be about 36,000 cal/gmole as compared to 12,500 cal/gmole for the liquid phase (4). The much higher gas phase activation energy could account for the low relative yield.

For xylose, the comparison between the phases is quite different. The reaction rate and activation energy at 3.9°C for liquid phase HF operation are listed by Selke as 0.184 min⁻¹ and 6,500 cal/gmole, respectively (4). The values for gas phase HF operation at 3.5°C are 0.636 min⁻¹ and 14,000 cal/gmole for the rate constant and activation energy, respectively. The liquid phase reaction achieves quantitative xylose yields after about 25 min (4). The gas phase HF reaction achieves these same quantitative xylose yields in about 5.5 minutes. The conclusion is that for xylose conversion, gas phase operation appears to be much better than liquid phase HF operation. The higher activation energy for the gas phase appears not to be a handicap for xylose production, for the reaction rate is still much higher than for liquid phase HF.

From the data, the xylose rate is much faster than the glucose rate at all temperatures. The explanation for this is simple. The xylose is present in the amorphous hemicellulose fraction of the wood. The majority of the

glucose is present in the rigid crystalline cellulose component. The HF more easily penetrates and disrupts the already nonuniform hemicellulose. The HF molecule is more easily allowed to orient itself for reaction with the xylan. The crystalline cellulose structure keeps the HF from positioning itself for reaction with the glucan component, hence the lower glucose conversion rate.

Figures 9 and 10 show HPLC chromatographs using pure HF for 5 and 70 seconds reaction time, respectively. The large mass of nondistinct peaks at the 8-12 minute mark correspond to a degree of polymerization (DP) of at least 5 or 6. All higher oligomers appear to void the column at this time as well. As the reaction proceeds, the xylan reacts first, and the quenched samples give, almost exclusively, peaks at 10 minutes. Therefore, the larger reversion oligomers tend to form first with only minimal xylose monomer. As the reaction progresses, glucan begins to react; xylan continues to react. The reversion products begin to produce a distribution of various oligomers with a substantial amount of both xylose and glucose monomer. The above analysis is quite different from that of liquid phase samples where the reverse scenario appears to occur. At short reaction times, monomeric sugars are first formed in the liquid phase system. As the reaction progresses, the oligomeric distribution expands toward larger DPs. Therefore, reaction in the liquid phase appears to cleave sugar units at the end of chains while reaction in the gas phase appears to cleave,

at least initially, bonds within the chains. The oligomeric distribution could be an important factor in the future if microorganisms capable of digesting these mixtures are developed. The optimum distribution would then be that mixture of oligomers most easily converted to ethanol.

As stated previously, mass transfer effects were initially assumed to be the sugar conversion controlling process. This idea was negated, for the conditions investigated, with the first yield results. The virtually quantitative xylose yields at short reaction times alluded to negligible mass transfer limitations. The much lower glucose yields for the same reaction time reinforced this assertion. If mass transfer effects were important, one would expect the xylose and glucose fractional yields to be more equal, and Figures 2-6 obviously show the yields are not equal.

The promising economic outlook for HF saccharification, both liquid and gas phase, justifies continued effort toward the elucidation of fundamental process data. Alternative technologies for the same fuels-and-chemicals endpoint pale in comparison. The after-tax return (Table 2) is sufficiently high, especially for gas phase HF, that serious effort toward industrial application of this relatively new technology should commence very soon.

SUMMARY AND CONCLUSIONS

Though hydrogen fluoride saccharification is a relatively new technology and lags behind other competing hydrolysis methods in regard to technological development, research continues on many aspects of both liquid and gas phase operation. Each new piece of information tends to reinforce the assertion that HF saccharification is the method of choice for the conversion of lignocellulose to liquid fuels and chemicals. The economics, yields, and efficiencies all appear quite favorable.

For pure HF at approximately room temperature, essentially quantitative yields are obtained for xylose and quite high yields for glucose after only about two minutes reaction time, at least with the small sample size used in these studies. Though the glucose conversion rate tends to drop much more rapidly with decreasing temperature than does the corresponding xylose rate, near quantitative yields of xylose and approximately 74% yields of glucose can still be achieved at 20°C in as little as 3.5 minutes. At lower temperatures, the time necessary to achieve high glucose yields was too long to ascertain using the available experimental system. However, virtually theoretical yields

of xylose were obtained even at the lowest temperature (about 3.5°C) in only about 5.5 minutes.

From the above discussion, it can be concluded that a dilute gas phase HF flow (low temperature) may be a good method for the prehydrolysis of lignocellulose to remove the hemicellulose fraction from wood samples, as long as the reaction time is kept sufficiently short to minimize glucose formation. The method of choice, as used by Hoechst (15), has previously been a dilute sulfuric acid prehydrolysis. Research must continue in order to determine if this is an economically valid assertion.

The first-order reaction model appears to fit the data reasonably well for xylose but not for glucose. Varying the HF/N₂ ratio can be considered to generally affect only the system operating temperature for xylose. For glucose, the correct reaction model must incorporate into it some function of HF concentration. The proposed rate constants and activation energy obtained using the simple first-order model may therefore be somewhat in error for glucose.

The HPLC analysis of the gas phase reaction samples is somewhat different from those performed on liquid phase HF saccharification samples. The liquid phase samples tended to first form monomer, then progressively form oligomers of higher DP. The xylose would remain almost completely in monomeric form. For the gas phase samples, however, the first sugars to be formed (after quenching) were of DP on the order of 5 or 6. With increasing reaction times, other

smaller oligomers as well as some monomer were formed. The xylose remained mostly in oligomeric, not monomer form. In the liquid phase reaction, the glucose units are cleaved from the end of cellulose chains yielding initially glucose monomer. Gas phase reaction, on the other hand, results in internal cellulose chain bonds being broken, thus initially giving relatively large DP glucose chain products.

This work represents a first pass at the gas phase kinetics of HF saccharification. Though a great deal remains to be investigated, the kinetics appear at this time to be quite favorable. Saccharification at room temperature using pure HF will be a quick, efficient, and non-energy intensive process for the production of sugars (and later liquid fuels and chemicals) from a lignocellulosic feedstock. Other temperatures and flow concentrations may require more cooling and/or heating requirements, but may also reduce HF losses. The optimum conditions have yet to be determined.

RECOMMENDATIONS

The gas phase HF studies presented in this paper represent only preliminary investigations. In order for the data to be of practical industrial importance, a great deal more information concerning more than just the gas phase kinetics of HF saccharification needs to be elucidated. This includes more information on such things as yields under various conditions, sorption characteristics, and system modeling.

The studies performed initially assumed that varying the HF/N₂ flow ratio merely changed the system temperature, and that any other effects were negligible in comparison. This was found to generally be the case for xylose but not for glucose. In order to conclusively determine whether or not this assertion is correct even for xylose, the temperature effects need to be uncoupled from possible flow composition effects. The existing apparatus could be modified to accomplish this goal by adding a coiled flow tube before the reactor inlet. The coil could be submerged in a constant temperature bath. As long as sufficient length is provided, the outlet temperature of the HF stream could be accurately controlled. The HF/N₂ temperature could

then be altered without altering the actual compositions, while the reverse would also be true.

In addition to studying yields at different temperatures, yields at various operating pressures should also be investigated. The experimental setup used in these studies was not designed to accomodate pressure changes. Therefore, for changes in this parameter, a completely new reactor system must be designed.

The sample size used in this study was sufficiently small to eliminate mass transfer effects, or at least to make them so small as to be negligible. The point at which mass transfer effects become important can be determined by analyzing yield data from runs using increasingly thicker samples. This point is economically important for industrial applications. The largest raw wood size possible, while still minimizing mass transfer limitations, would be cost efficient due to reduced chipping requirements.

At the conditions discussed in this paper, mass transfer limitations appear unimportant, but with increasingly larger sample size they will become important. Therefore, it would be desirable to develop a model which would account for both reaction rate and mass transfer effects. This comprehensive model would then be valid at all reaction conditions. But in order for this model to emerge, a great deal more fundamental information concerning various rate processes must be obtained.

Degradation of sugars can occur during posthydrolysis. Therefore, microorganisms capable of converting the oligomeric sugar mixture to ethanol should be developed. Process hardware requirements would thus be simplified. For this development to be possible, the oligomeric distribution of various sugars must be determined. Those reaction conditions yielding the most easily fermentable oligomeric mixture would be desirable.

Sorption studies need to be performed in order to help determine the extent of reaction as the reaction is actually progressing, not after it has been quenched. The sorption studies are also very important in determining the HF recycle efficiencies and costs under industrial HF saccharification applications.

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