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THE KINETICS OF HYDROGEN FLUORIDE SACCHARIFICATION OF CELLULOSE

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THE KINETICS OF HYDROGEN FLUORIDE SACCHARIFICATION OF CELLULOSE

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ABSTRACT

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HF saccharification of lignocellulosic materials can produce sugars as a source of liquid fuels and chemicals from a renewable substrate, and has advantages over alternative technologies in high yields with short reaction times at near ambient conditions, efficient HF recycle, and only minor pretreatment requirements. Reaction with standard-sized wood chips is modeled as two dimensional mass transfer with diffusivity much larger in the direction of the pores. Reaction of crystalline and of amorphous cellulose to produce either water-soluble products or HF-soluble intermediates which then further react to give water-soluble products is incorporated. To permit the determination of some reaction parameters, this model is simplified by reducing the particle size to eliminate mass transfer and heat transfer resistances and by simplifying the reaction scheme to cellulose undergoing first solubilization in HF and then reaction to form water-soluble products. Rate data for production of water-soluble sugars is presented as a function of temperature between $-13^{0}C$ and $5^{o}C$ and of

water concentration between anhydrous and 6.4% water in % of the HF by weight. A pseudo-first order model is found to require an "initial delay" parameter representing solubilization time, especially at low temperatures. This parameter approaches zero at temperatures above 0-5^{o}C. Increasing water concentration slows the reaction rate. Activation energies for the first order reaction of cellulose with HF are found to be 12-34 kcal/mole. The reaction with wood is slower than with filter paper. For wood at room temperature with anhydrous HF, a reaction time of 10 minutes is predicted to provide ample time for complete reaction of small chips. For standard sized (3x3x.5 cm) wood chips, mass transfer limitations become important.

To Barry, Lori, Erik and Jill

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I. INTRODUCTION

The study of HF saccharification began at Michigan State University four years ago in the aftermath of the Arab oil embargo and the resultant escalation in petroleum prices which led to a considerable interest in renewable sources of energy. Subsequent drops in oil prices due to decreased demand, caused in part by efforts at conservation but unfortunately due in large measure to the recent world-wide recession, led to a shortsighted decrease in interest in and funding for such projects.

The fact remains that the world's supply of petroleum is finite. There has been argument over when the supply of oil will run out, but there can be no argument that that day will come if our technological society endures and continues to utilize petroleum as a primary source of fuel and chemicals.

Major efforts have been directed toward replacing oil with coal, and though these efforts, as mentioned above, have experienced a decline in interest and funding difficulties, research into coal gasification and liquefaction is proceeding. Coal as a fuel for power plants and industry has experienced a resurgence, due primarily to the increase in cost of natural gas. At this university, a power plant

which had recently been converted to natural gas was reconverted to coal. Use of coal as a source of chemicals and liquid fuels still awaits a great deal of needed research. However, reliance on coal as a substitute for petroleum has a fundamental flaw - coal, like petroleum, is a nonrenewable resource. When the supply of coal becomes depleted, we will find ourselves again facing the problem of replacing our energy and chemical sources. In addition, there are considerable difficulties associated with adequate protection of the environment if use of coal increases substantially. These range from concerns about strip mining to the unknown consequences of increasing the carbon dioxide content of the atmosphere.

As a consequence of these problems, we feel that use of renewable sources for energy and chemicals to replace nonrenewable sources will eventually be imperative and already is advantageous under certain circumstances. If this is the case, then it is important to conduct the research needed to develop these renewable sources so they can be utilized as they become economically or politically advantageous.

There are a variety of options for providing power in the form of electricity and for providing heat, including nuclear fission or fusion, solar power, hydroelectric power, geothermal energy and others. What these processes cannot

easily provide is a source of liquid fuels, and perhaps even more important, a source of raw materials for the chemical process industries. It is in this area that we feel utilization of biomass can make a significant contribution.

Biomass consists of two major chemical groups. The cellulosic fraction consists of chains of five- and six-carbon sugar residues. When these are hydrolyzed to free sugars, existing (in fact ancient) technology can be utilized to ferment the six-carbon sugars to ethanol or to various other products. Methods now under development can ferment the five-carbon sugars to a variety of products, including ethanol (Chambers et al, 1979; Chiang et al, 1981; Funk, 1975; Jeffries, 1981; Rosenberg, 1980; Rosenberg et al, 1981; Veeraraghaven et al, 1979). The ethanol can be utilized directly as a liquid fuel, or it can be converted, again with existing technology, to ethylene or butadiene for use as chemical raw materials (Goldstein, 1975, 1976). The lignin fraction of the biomass is a very complex polymer containing a variety of aromatic groups. It can be utilized to produce phenol or other aromatic compounds. This conversion has been shown to be feasible (Goheen, 1966) but has not yet been refined due to lack of economic incentive in comparison with cheap oil. As an indication of the importance of ethylene, butadiene and phenol as chemical

raw materials, it should be noted that 95% of all synthetic polymers can be derived from these three raw materials alone (Goldstein, 1975).

Therefore if biomass can be broken down into its sugar and phenolic components, it can be a valuable source of both liquid fuels and chemicals. Biomass also has the important property of being a renewable source for these valuable materials. With proper management, biomass can be produced indefinitely and with little if any detrimental effect on the environment. Even release of carbon dioxide into the atmosphere during fermentation need not be a concern, since the replacement biomass being grown will remove it again.

The major problem in reliance on biomass as a renewable energy source is that, though renewable, it is a finite resource. Agricultural land is needed for food production, and a considerable amount of land is utilized for homes, parks, factories, schools, etc. Large portions of land are not suitable for biomass production because of being too cold, too dry, inaccessible to harvest, or other problems. Proper management of "energy forests" or other biomass production land can significantly increase the rate of biomass production, but even optimistic estimates do not claim that biomass can provide all our energy needs. For instance, a report by the U.S. Congress Office of Technology

Assessment (1980) estimated that with "high development" biomass could supply 12-17 Quads of energy per year by the year 2000, which is 15-20% of current U.S. energy consumption. Therefore we feel biomass will be most valuable in the long term as a source of chemical raw materials and of liquid fuels, the uses not easily provided by alternative renewable energy sources. This is the basis of our contention that eventually biomass may be too valuable to burn (Selke et al, 1982). Quantitative predictions of biomass availability are discussed further in Appendix A.

The major obstacle to the utilization of biomass for chemicals and liquid fuels is the development of effective conversion processes for obtaining the sugars and phenolics contained in the biomass. The best conversion process will be the one which produces high yields of both types of products at a reasonable cost. Yield especially is crucial due to the limited supply of biomass, as discussed above, and is closely tied to cost through the cost of the biomass raw material. My discussion here will focus primarily on the production of sugars from the cellulosic portion of biomass. Production of phenolics and other chemical raw materials from the lignin fraction is a major research area in its own right, one which is likely to be even more complex than cellulose hydrolysis. Our major concern with lignin in regard to cellulose hydrolysis is that a hydrolysis

procedure that does not significantly diminish the value of lignin as a source of chemical raw materials has a significant advantage over one which causes a large amount of condensation of the lignin, leaving it suitable for little use other than burning as a solid fuel.

We have described elsewhere (Hawley et al, 1983) some of the history of biomass saccharification, have compared some of the major saccharification technologies currently under investigation, and have discussed our reasons for feeling that saccharification using hydrogen fluoride is potentially best. Concentrated acid processes utilizing HCl or H_2SO_4 have the advantages of high sugar yields, short reaction times, and the use of essentially ambient conditions for the reaction. Their disadvantages are high acid consumption, expensive acid recovery and recycle, severe corrosion problems, and the requirement of prehydrolysis with dilute acid followed by drying of the very wet substrate. Dilute acid (H_2SO_4) processes are generally cheaper than concentrated acid or enzymatic processes, but require high temperatures and pressures, have relatively low yields, and result in considerable sugar degradation, which contaminates the product sugar solution and can inhibit fermentation. Enzymatic saccharification is currently very expensive, requires long reaction times and extensive pretreatment of the substrate, and has relatively low yields,

though the product sugars obtained are quite pure. Hydrogen fluoride saccharification shares the advantages of high sugar yields, short reaction times, and the use of essentially ambient reaction conditions with the other concentrated acid processes. However it does not require prehydrolysis, and hence does not require the drying of a very wet prehydrolyzed substrate. Corrosion problems are significantly less than for other concentrated acid processes, and HF is easily removed from the reaction mixture by vaporization, so recovery and recycle will be relatively easy and inexpensive.

A preliminary comparison of costs of HF saccharification with the leading alternative technologies, dilute acid and enzymatic hydrolysis, was encouraging (Selke et al, 1982). Due primarily to the high yield of glucose from HF saccharification, costs for raw materials and chemicals were estimated as 5.4¢/lb glucose, compared to 5.5-6.2¢/lb for dilute sulfuric acid hydrolysis and 9.2¢/lb for enzymatic hydrolysis. The wood cost used for these estimates was $40/dry ton. Higher wood costs would increase the price advantage of HF hydrolysis over the alternative processes. While these figures include only feedstock and chemical costs, equipment and utility costs for HF saccharification should be comparable to or less than those for the alternative processes, since most of the equipment used

will be carbon steel, and near ambient temperatures and pressures will be utilized for the reaction as well as for HF recycle. HF boils at 19.54°C and has a heat of vaporization of less than 1800 cal/20.01 g (Simons, 1950). In contrast dilute acid hydrolysis requires high temperatures and pressures, as well as a prehydrolysis before the main hydrolysis. Enzymatic hydrolysis requires elaborate and extensive pretreatment of the substrate, very long reaction times, and a large and complex enzyme production system.

Our research at Michigan State has focused on only two substrates. Populus grandidentata, Bigtooth aspen, was selected as representative of several species of hybrid poplar being developed for possible use in "energy plantations." These trees have been selected because of their rapid growth and their ability to coppice, to grow again from the stump after being harvested. We have also used filter paper as a substrate, as a source of essentially pure cellulose.

The research discussed here is devoted primarily to exploring the reaction conditions required for HF saccharification and the development of a kinetic model which can be utilized in the design of a reaction system.

First the early German work on HF hydrolysis and the recent work at Michigan State and elsewhere will be summarized. Next a general description of wood structure will

be presented, followed by a discussion of the available kinetic information for other acid hydrolysis processes and a brief discussion of enzymatic hydrolysis kinetics. A conceptual model for HF saccharification will be developed and then the current experimental results will be presented and discussed. Finally there will be a discussion of the next stage of research needed for the further development of an HF saccharification process.

II. HF SACCHARIFICATION

A. EARLY WORK

J. Gore noted in 1869 that HF transformed paper and other cellulosic materials into "glutinous substances" and dissolved them (Gore, 1869). The first real investigation of this reaction was in 1929 by Helferich and Bottger, who found polyglucans were obtained when cellulose was treated with anhydrous HF, and that these polyglucans could be converted to glucose by boiling with dilute acid (Helferich and Bottger, 1929).

In 1933 Fredenhagen and Cadenbach studied the mechanism of the reaction of HF and cellulose and claimed, on the basis of boiling point and conductivity measurements, that it involved the formation of glucosyl fluorides, which in HF solution react with even small quantities of water to produce glucose and regenerate the HF (Fredenhagen and Cadenbach, 1933). During precipitation or evaporation of the HF, polyglucans were formed, which could be reconverted to glucose by boiling in dilute acid. They then studied the saccharification of wood using HF. They suggested treatment with anhydrous or highly concentrated HF as a good quick method for determination of carbohydrate and

lignin content of wood, straw, and other lignocellulosic materials. They reported that the reaction slows down with increasing water concentration, 95% HF requiring only "a few minutes", 80% HF requiring longer than an hour and an increase in temperature, and 70% HF having no effect on cellulose. They also studied the reaction of cellulose with HF gas, stating that it transformed cellulose into water-soluble substances as long as the temperature was low enough for a liquid adsorption phase to be formed. A smaller amount (1:1) of HF to wood could be used in the gas phase reaction, with up to 95% yield. A study of the reaction thermodynamics revealed that 94 gram calories of heat were released during the reaction of one gram of well-dried spruce with an excess of liquid HF. In further study of the gas-phase reaction, they demonstrated that almost 99% of the HF could be recovered from the reaction products by vacuum or flue evaporation accompanied by slow heating to 100^{o}C, and then recycled for use on fresh wood. The polyglucan products were recovered by washing the solid residue with water. Recovery of polyglucan was greater when the reaction had been carried out with a small amount of water (greater than 0% but less than 2% of the acid or wood). This was attributed to decreased repolymerization of the sugars when some water was present. They stated that the theoretical maximum yield was always obtained if

the reaction product was boiled in dilute acid (0.02 N) to solubilize all the polyglucans. Water content greater than 2% reduced the HF gas pressure and made its removal more difficult. They recommended that a small amount of HF be left in the reaction mixture, as this facilitated solubilization of the polyglucan product. This excess HF was then removed by precipitation with calcium carbonate and the product sugars obtained, after filtration, by vacuum evaporation. They further reported that this process was tested in an industrial institute and was patented (Fredenhagen and Cadenbach, 1933).

A patent issued in Germany in 1933 for saccharification of wood with hydrogen flouride listed as discoverers of the process Georg Pfleiderer and Ernst Koch, who apparently worked with Fredenhagen and Cadenbach (Pfleiderer and Koch, 1933). It provided for sawdust or wood chips to be fed continuously into a long rotating cylindrical tube, with air being blown in from the other end. The wood is contacted with HF in the first compartment of the tube, which has a cooling jacket to keep the temperature below the condensation temperature of HF. Saccharification takes place and then the wood, containing HF, is transported by a helical thread into the second part of the container which may be divided into several compartments and is covered with a heating jacket. Here the HF is vaporized and blown back into the

first compartment by the air stream, which has been previously heated for best results, and is taken up by fresh wood. The air escapes through the opening where the wood enters. If a longer reaction time is desired, a third stage can be inserted between the first two which is maintained at a temperature favorable to saccharification. The HF removed in the third stage would then be diverted around this second stage to go directly to the first compartment. Another option is the removal of some of the HF before heating the mixture, with the HF from the heated and the unheated compartments either combined or reintroduced to the first compartment at separate points. The hot HF/air mixture could also be cooled prior to reintroduction. Another option mentioned was using separate but connected containers rather than a single vessel. It was claimed that with careful regulation of the air flow no HF was lost with the air through the wood entrance, and loss with the saccharified wood at the exit was very small. Small additions of make-up HF could be made by mixing it with the air beween the first and second compartments. They further pointed out that any HF that did escape with the air flow could be recovered and reintroduced to the reaction vessel by recycling the air.

The next development in HF saccharification was a modification of the process described above by two Austrian

inventors, Hoch and Bohunek, which used pure gaseous HF at a reduced pressure. Wood chips dried to a 5-6% water content are treated with 35 parts HF to 100 parts cellulose at a pressure of 30mm Hg. After about 30 minutes the reaction is complete and the HF is recovered by further reducing the pressure and raising the temperature while the wood is kept in continual motion. Contaminating acetic acid is removed from the HF by condensation, and the HF gas is then recycled. The reaction products are separated into lignin and soluble sugars by boiling in water for 15 minutes. Pressure is increased and a small amount of acid is added if necessary. It was claimed that 90% of the cellulose was saccharified and 80% of it could be recovered for further processing. It was also stated that the wood particle size could be larger than that required for the Fredenhagen-Helferich process because HF penetrated so deeply at the reduced pressure, thus reducing the space and input energy requirements (Luers, 1937).

A later report on the work of Hoch and Bohunek stated that in comparison of HF saccharification with other gaseous mineral acids, HF was the best. The reversion of glucose to polyglucans was found to be dependent on temperature, length of the reaction, concentration, and quantity of HF, and could be kept to a minimum, thus increasing the yield of low molecular weight, uniform reaction products, and

increasing the amount of water taken up in the reaction without decreasing the HF concentration. Their process was widely patented in Europe, and they operated a pilot plant for six months in Upper Bavaria to judge the technical feasibility of the process. They reported that the optimal water concent of the wood was 2-3% and of the HF less than 5%. The optimum HF:wood ratio was 40 kg to 100 kg dried wood. The HF was introduced at a temperature of 35-40^{o}C, with a partial vacuum maintained at all times. After the wood had been completely penetrated, the HF was condensed by lowering the temperature. After reaction had occurred, some of the HF was removed by low pressure at normal temperatures, and the rest by maintaining the low pressure and heating the reaction products to a maximum of 62^{o}C. HF recycle was satisfactory, with contaminating acetic acid easily removed by condensation. The reaction product had an HF content of about 1%, but this could be reduced by a longer degassing time. The reaction products had a smooth black shiny appearance, rather like coal. The wood chips kept their original shape and when broken showed that the reaction had occurred throughout the chip. A second hydrolysis with 2% sulfuric acid at 130-135^{o}C for 30-45 minutes in a pressure extractor was used to convert the polysaccharides to monomeric sugars, and the sugar solution was separated from the brown lignin by filtration.

If monomeric sugars were not required, the water-soluble oligomers were extracted with water in a pressure extractor utilizing the traces of acid already present. The acidic sugar solutions were neutralized with lime and filtered. Average yields were reported of (a) from pine, yield of 65% raw carbohydrates, 50% reducing sugars, (b) from beech, yield of 65% raw carbohydrates, 57% reducing sugars, all based on wood dry weight. The fermentability of the sugars was reported to be the same as sugar produced by the Scholler or Bergius processes. It was further reported that pentosan-rich materials such as hemp were also successfully hydrolyzed by this method. It was mentioned that with beech wood, a fractionated second hydrolysis of the reaction products satisfactorily separated pentoses from hexoses, but no details of the procedure were given. Most of the process equipment used was iron, with copper, bronze, Monel or aluminum/bronze used for some applications, with negligible corrosion. Energy input was low, and sugar yields satisfactory (Luers, 1938).

In the late 1950's the hydrolysis of cotton linters with 80-100% HF at 10-30^{o}C was studied in the Soviet Union by Rogovin and Pogosov. They found the hydrolysis was slow at lower concentrations but was completed in 5-10 minutes with 95-100% HF. Water-soluble sugar oligomers with a degree of polymerization (DP) of 15 to 17 were formed.

HF:cotton ratios of 1:1 and 0.5:1 produced water-soluble products in reactions at 40-50°C for 10-20 minutes without stirring. HF was removed by applying a 25-35 mm Hg vacuum at 40-50°C for 30 minutes, leaving a residual HF content of 1.3-1.5% of the cellulose, which was then removed by precipitation as CaF_2. Comparison of the products from hydrolysis of cotton linters and polycondensation of glucose in 93% HF showed the products to be identical with respect to degree of polymerization and specific rotation, and the basic bonds between the monomeric units were identified as α-1-6 bonds (Rogovin and Pogosov, 1958, 1959).

With the exception of this work and a limited amount of further investigation in the Soviet Union, it appears that HF saccharification was virtually ignored until 1979, when our group at Michigan State University and several researchers in Europe rediscovered the process at approximately the same time.

B. WORK AT MICHIGAN STATE UNIVERSITY

The study of biomass saccharification using hydrogen fluoride at Michigan State University grew out of work on the structure of cell wall glycoproteins in Dr. Derek Lamport's laboratory, in which HF was used as a deglycosylation reagent which rapidly cleaved all o-glycosidic linkages while leaving peptide bonds intact (Mort and Lamport, 1977). When it was realized that these are exactly the bonds which are cleaved in the hydrolysis of cellulose to glucose, and rising gasoline prices subsequent to the Arab oil embargo led to renewed interest in ethanol from biomass, the old German work was rediscovered and laboratory work in Dr. Lamport's lab in the MSU/DOE Plant Research Laboratory was begun to confirm the German work and expand on it. Up to this point, our work has concentrated on the liquid phase reaction.

The first efforts were directed toward determining sugar yield and exploring HF removal by vacuum evaporation as a function of water concentration, evacuation time, and evacuation temperature. Virtually quantitative sugar yields were obtained from the reaction of filter paper with HF at room temperature for one hour with water concentrations of 0-3.5% of the HF by weight. At 0 ^{o}C yields were slightly less than quantitative, and were higher when a small amount of water was present than when the reaction

was anhydrous. Sugar yields from poplar wood chips ranged from 0.4 to 0.8 g total soluble sugars per g wood chips, depending on the reaction conditions. The lowest yields were obtained at a very high water concentration (25%) with yields from 90-100% HF ranging from 0.6 to 0.8 g/g wood chips (Selke et al, 1982). Reaction times other than one hour were not explored in these early studies.

Another major part of our early research at Michigan State was directed toward HF removal. Because of our laboratory setup, the amount of HF added to the reaction vessel and the amount removed were not easily quantified, but it was possible to accurately measure the fluoride content of the reaction products after HF removal. Fluoride retention in the soluble (sugar) fraction was measured with on Orion combination fluoride electrode, and in the insoluble (lignin) fraction with the fluoride electrode after alkaline ashing to free any bound fluoride. Fluoride retention was found to depend on evacuation time, temperature, and reaction water content. With time held constant at one hour, fluoride retention decreased exponentially with increasing temperature until reaching a limiting value. With temperature held constant at 100^{o}C, fluoride retention decreased as evacuation time was increased to 2 hours, with extension of evacuation time to 5 hours giving no significant improvement. With time and temperature constant,

fluoride retention decreased with increasing water concentration up to 5% water by volume. The lowest fluoride retention attained for the sugar fraction was 4 mg/g wood. Fluoride retention in the lignin fraction was reduced to 0.1 mg/g wood after washing and dialysis, indicating that the lignin is not significantly fluorinated. An ashing of unreacted wood yielded 7 mg total ash per g wood, which in comparison with the fluoride retention lends support to our theory that the primary source of HF loss is due to the formation of fluorides from the metals in the wood ash. (Lamport et al, 1981; Selke et al, 1982; Hardt and Lamport, 1982a)

Another series of experiments dealt with determining the amount of reversion to oligomers which occurred during the reaction and during HF removal. An average degree of polymerization (DP) of about 6 was found after a one hour or more evacuation at 100^{o}C, with only 10-20% of the sugar in monomer form. In contrast, termination of the reaction by precipitation of the HF with calcium carbonate yielded 60-70% sugar monomer and 25-30% dimer (Hardt and Lamport, 1982a).

In other experiments, the glucosyl fluoride and xylosyl fluoride intermediates claimed by Fredenhagen and Cadenbach were isolated and positively identified by paper chromatography combined with gas chromatography-mass spectrometry

(Hardt and Lamport, 1982a, 1982b).

Material balance experiments were conducted to determine whether we could account for all the wood mass after HF reaction. 90-98% of the original mass was accounted for as the sum of the water-soluble and insoluble fractions. We determined that 10.8-12.8% of the weight of the water-soluble fraction could not be accounted for as sugars, and may be primarily water-soluble lignin (Clark, 1962; Selke et al, 1983). Acetic acid in the amount of 1.5-5% of the weight of the wood is produced by hydrolysis of acetyl groups in the wood (Harris, 1949) and would appear in either the vapor phase or with the sugars, depending on the evacuation conditions.

The major portion of our recent work has dealt with the determination of the necessary reaction conditions, modeling, and determination of kinetic parameters, and will be discussed in Sections V-VII.

C. RECENT WORK BY OTHER INVESTIGATORS

The other work done in the United States was by Andrew Mort (formerly a student of Dr. Lamport at Michigan State) and Susan Parker at the Charles F. Kettering Research Laboratory. They also studied the liquid phase reaction, using primarily pure cellulose, but also exploring the reaction with wood chips, corn stover, sawdust, and the cellulosic fraction of garbage. Studies of the sugar linkages in the oligomeric products showed few if any of the cellulosic β-1-4 linkages remaining. Most or all of the bonds were α, with 1-6 linked the most common but all linkages present. Studies on the percentage of monomeric sugars formed relative to sugar oligomers showed monomer concentration increases with a decrease in sugar concentration in the HF and with an increase in water concentration. Studies on reaction kinetics showed that at $0^{o}C$ the reaction was incomplete after 5 minutes but complete within 15 minutes, while at $24^{o}C$ it was complete within 3 minutes and at $-23^{o}C$ it was very slow, yielding only a small portion of water-soluble products. No sugar degradation was found, as glucose could be quantitatively recovered after all HF treatments (Mort and Parker, 1983).

In Europe, Defaye and Gadelle from France and Pederson from Denmark carried out research on the reaction of HF and cellulose (Whatman cellulose powder) using ^{13}C NMR

spectroscopy to characterize the reaction products. They found that 10 g cellulose dissolved in 15 ml HF at about -5°C for one hour gave, on precipitation with ether, a water-soluble product which was almost exclusively β-1-4 linked oligosaccharides, i.e. partially hydrolyzed cellulose, in a mixture of products with DP ranging from 1 to 10. A similar reaction at 20°C for one hour gave a different product, a mixture of oligomers having primarily α-linked glucose units. This same product was obtained when glucose was treated with HF under the same conditions. In dilute solution (10 g cellulose to 80 ml HF for one hour at 20°C) the main product obtained by precipitation with ether was glucosyl fluoride. When HF was evaporated from the dilute solution, the residue was an oligosaccharide mixture as obtained from the reaction at more concentrated conditions. The investigators conclude that in HF solution cellulose is completely degraded to α-D-glucopyranosyl fluoride which is in equilibrium with a mixture of sugar oligomers, with low concentration favoring the fluorides and high concentration favoring the oligomers. They also reacted pine with HF for 1 hour at room temperature and obtained a water-soluble product which was a mixture of glucose and sugar oligomers (Defaye et al, 1981).

Further experiments on the reaction of HF and cellulose showed that at -78°C cellulose did not dissolve at a

measurable rate. At -10°C it went into solution rapidly, and a 20% solution was obtained in about 5 minutes. Immediate cooling to -78°C and precipitation with ether showed the product to be largely insoluble in water, and ^{13}C-NMR showed this water-insoluble fraction to be β-1-4 linked glucopyranose oligomers (i.e. partially degraded cellulose). Treatment of cellulose with HF for 40 minutes at -5°C gave a water-soluble product which again contained β-1-4 linked glycopyranosyl residues. A 10% solution of cellulose in HF for 45 minutes at 20°C gave largely α-D-glucopyranosyl fluoride, while a 40-50% solution contained less fluoride and more sugar oligomers. When the HF was removed by evaporation with a stream of air from either the dilute or concentrated solutions, no glycosyl fluoride was obtained and the reaction product was largely α-linked oligomers with a preponderance of 1-6 linkages and a high degree of branching. Treatment of amylose (starch) and of glucose with HF gave the same products, α-D-glucopyranosyl fluoride or a mixture of acid-reversion products depending on the isolation procedure (precipitation with ether or HF evaporation). Treatment of D-xylose and 1-4-β-D-xylan with HF gave identical products which were nearly independent of the reaction and isolation procedures used, consisting of a complex mixture of oligosaccharides with little α-D-xylopyranosyl fluoride even in dilute solutions. Degradation of sugars

in acid solution yields furans, either 2-furaldehyde (furfural) from pentoses or 5-hydroxymethyl-2-furaldehyde from glucans. No detectable amounts of either were found, indicating there was little if any sugar degradation. The investigators state that anhydrous HF dissolves and depolymerizes polysaccharides, especially cellulose, more rapidly and at lower temperatures than any other acid that has been studied for this purpose. They suggest that this is due to the strong tendency of HF to form hydrogen bonds, which leads to the disruption of the intermolecular hydrogen-bonding of the polysaccharide molecules. They hypothesize that the subsequent formation of glycosyl fluorides takes place via protonation and formation of the conjugate acid and then of the oxocarbonium ion, which is the accepted mechanism for the acid-catalyzed hydrolysis of pyranosides, though pointing out that in the ^{13}C-NMR spectra they measured in HF solution, they did not observe oxocarbonium ions, only the sugar fluorides. They further suggest that the formation of the oligomeric reversion products follows the classical pathway of electrophilic reaction of an oxocarbonium fluoride intermediate with a polyhydroxylated carbohydrate residue. They point out that degradation of polysaccharides with HF according to the mechanism they proposed is <u>not</u> a hydrolysis, in contrast to the reaction in other aqueous acids (Defaye et al, 1983).

Thorkild Bentsen at the Biotechnical Institute in Kolding, Denmark, is studying the solvolysis of barley straw with anhydrous HF and is currently operating a small pilot plant. Both acid (0.6% H_2SO_4, 140°C, 1 hour) and enzymatic (α-amylose and amyloglucosidase, 55°C, 72 hours) posthydrolysis have been explored. The yield of fermentable sugars (20% xylose, 36% glucose based on dry mass of straw) was reported to be near the theoretical limit. The pilot plant procedure is for 35-40% by weight of HF gas to be absorbed by dry ground barley, wheat straw or dry beech wood chips (2-3% moisture) which are mechanically agitated. The reaction is then allowed to proceed for one hour at room temperature. In removing the HF, a carrier stream of inert gas (perchlorethylene C_2Cl_4) is introduced at a temperature of 80-100°C and is later separated from the HF gas by condensation. After a one hour time period, a recovery of 98.7% of the HF charge has been demonstrated. After either acid or enzymatic posthydrolysis, fermentation to ethanol with Saccharomyces cerevisiae has been demonstrated with no inhibition of fermentation (Bentsen, 1982).

Research on HF saccharification is also being carried out by Hoechst in Germany, but no information is available on their work.

III. WOOD STRUCTURE

Wood is both chemically and structurally a very complex material. This section will present a brief overview of some of the important aspects of wood structure, especially as it relates to hydrolysis.

First, trees native to the United States are divided into two classes, hardwoods or deciduous (angiosperms), and softwoods or evergreens (gymnosperms). Our research has dealt exclusively with poplar, a hardwood, so this description will concentrate on hardwood properties.

About 55% of the volume of a typical hardwood is made up of specialized vessels or pores which conduct sap. In the heartwood and inner sapwood of many hardwoods, the pores are filled with a frothlike growth called tyloses from the neighboring cells. The vessels are made up of relatively large cells, usually with open ends, though sometimes separated by a grating, set one above the other, forming open passages which extend for relatively long distances. Vessel cells, or segments, are typically 20-30 μm in width, though in some tree species they are as much as 330 μm. Lengths of vessel segments are 0.18 to 1.3 mm, and vessels themselves up to three meters have been found. (SERI, 1978; Tarkow et al, 1963; Thomas, 1977)

About 26% of the volume (though it can be as high as 67%) is tracheids, or fibers. These are the strength-giving elements, and generally are smaller cells with small cavities and relatively thick walls. They are generally elongated with closed pointed ends. Average length is slightly less than 2 mm, but they can range from 0.7 to 3 mm. Diameter is generally less than 20 μm. Thin places in the walls of the fibers and pores, called pits, allow the passage of sap from one cavity to another.

About 18% of the wood (ranging from 10-40%) is wood rays, strips of brick-shaped horizontal parenchyma cells extending in a radial direction. These store starch and other food in the sapwood and distribute it horizontally. In the heartwood they contain extractives. Width of the rays varies from one to over fifty cells. Longitudinal rays also occur in hardwoods.

All of these cells are cemented together by a thin layer called the middle lamella. It is this layer which is dissolved in pulping, allowing the fibers to be separated. (SERI, 1979; Tarkow et al, 1963; Thomas, 1977)

Chemically, wood consists of five fractions. The three major components are cellulose, hemicellulose and lignin. The remainder of the wood is extractives and ash.

Extractives can account for 4% to over 20% of the weight of the wood. They contain a large variety of

compounds, including volatile oils such as terpenes, resins, fatty acids, waxes, flavonols, pyrones, anthranols, tannins, and water-soluble carbohydrates.

Ash concentration can vary from 0.2 up to 8% or more. The higher ash contents are usually found in tropical woods. Most domestic wood contains 0.2-1.0% ash. The bulk of the ash is composed of CaO, K_2O, MgO and SiO_2. Fe_2O_3, P_2O_5, SO_3 and Cl are also found, but usually in lesser amounts. Typically half the ash is CaO and 20% K_2O. Aluminum, lead, zinc, copper, titanium, tin, nickel and thallium have also been found in trace amounts in wood ash. (SERI, 1979; Tarkow et al, 1963)

The carbohydrate and lignin content of wood is usually reported as a percentage of extractive-free wood. Lignin is generally 18-28% of the weight of the wood, higher in softwoods than in hardwoods, and is present in the middle lamella and in the cell wall. It is a three-dimensional polymer based primarily on the phenylpropane unit, which is deposited in an amorphous state surrounding the cellulose fibers. It is generally agreed that ether bonds are formed to some extent between the lignin and the hemicellulose. The actual chemical structure of lignin is exceedingly complex. It is usually defined operationally as that portion of the wood that is insoluble in 72% sulfuric acid. (SERI, 1977; Tarkow et al, 1963; Thomas, 1977)

Carbohydrates account for 65-75% of the weight of the wood. Holocellulose is classified according to either of two schemes. The most common distinguishes between cellulose and hemicellulose, which is defined as the easily hydrolyzed portion of the cellulose. The other classification refers to α-, β-, and γ-cellulose, based on solubility in alkali. α-cellulose is insoluble in 17.5% sodium hydroxide. β- is soluble, but is precipitated by acidification, and γ- is the soluble portion which is not precipitated by acid. (SERI, 1979; Tarkow et al, 1963)

Cellulose, which is 40-44% of the weight of the wood in softwoods and 43-47% in hardwoods, consists primarily of glucose residues joined by β-1-4 glycosidic linkages. It also contains traces of mannan and xylan. The polymers form thread-like chains of molecular weight greater than 100,000. These chains can be woven together in a random manner, in amorphous cellulose, or can fit together in a crystalline arrangement. The rigidity of crystalline cellulose arises from the arrangement of the ether linkages, yielding a stiff and extended chain, and from both intra- and inter-molecular hydrogen bonding (SERI, 1979; Tarkow et al, 1963; Thomas, 1977). Blackwell's analysis (1980) of the X-ray diffraction patterns for cellulose showed a monoclinic unit cell containing cellobiose residues of two chains. Two intramolecular hydrogen bonds are formed:

O3'-H•••O5 and O2-H•••O6', and inter-molecular O6-H•••O3 hydrogen bonds are formed with the next chain in the 020 plane, yielding a structure that is a series of staggered hydrogen-bonded sheets of parallel chains. This structure rules out the folded-chain models postulated in the past. X-ray diffraction measurements show the crystalline portions of cellulose to be about 600 Å in length, joined by amorphous regions in a repeating pattern (Thomas, 1977).

Hemicellulose is 25-29% of the weight of softwoods and 25-35% of hardwoods. It is composed primarily of branched molecules containing 50-200 sugar units, usually of several different kinds, including D-glucose, D-galactose, D-xylose, D-mannose, L-arabinose, 4-O-methyl-D-glucuronic acid and lesser amounts of L-rhamnose, L-fucose, and various O-methylated neutral sugars. There is significant variation in composition and structure of hemicellulose among plant and tree species. In general, softwood hemicellulose is primarily mannan, while hardwood hemicellulose is primarily xylan. Softwoods contain more galactan than do hardwoods. The difference in structure between cellulose and hemicellulose renders hemicellulose less able to form regular highly hydrogen-bonded crystalline regions, so its structure is generally amorphous and it is considerably more soluble and more easily hydrolyzed (Polglase, 1955; SERI, 1979; Thomas, 1977; Whistler and Zysk, 1978).

Hardwood hemicellulose is generally composed of β-1-4 linked D-xylopyranose chain units, with 4-O-methyl-D-glucopyranosyluronic acid units joined by α-1-2 linkages, usually at the rate of one side chain per ten D-xylose units. On acid hydrolysis, high yields of 2-O-(4-O-methyl-α-D-glycopyranosyluronic acid)-D-xylose are always obtained as this aldobiouronic acid is quite stable to acid hydrolysis. Acetyl groups occur in wood in the range of 3-17% of the wood, with the highest content in hardwoods. The average is 7.1 ester groups per ten D-xylose units, with most attached to C-3 and the rest to C-2 of the D-xylose residues.

Hemicellulose is sometimes divided into a more linear less acidic A portion, which can be extracted with alkali and precipitated by neutralization, and a more acidic and branched remainder, called the B portion, which is precipitated with ethanol from the neutralized alkali extract.

The distribution of the chemical components in the cell is not uniform. The typical structure of a woody plant cell is as follows. When it is produced by cell division, the cell consists of a primary wall, which can grow in length and width. When it has reached full size, a secondary wall is deposited on the inside of the primary wall, adding thickness and rigidity. Cells are joined to adjacent cells by the middle lamella. The term compound middle

lamella refers to the middle lamella itself plus the two adjacent primary cell walls, and is often used since the primary cell walls themselves are too thin (less than 1% of the cell wall) to be easily observed. Adjacent to this is the first layer of the secondary cell wall called the S1 layer. It makes up 10-22% of the wall thickness. Next is the central S2 layer, which is the largest, 70-90% of the wall thickness, and then the inner S3 layer, which is adjacent to the lumen and is the thinnest, 2-8% of the wall, of the secondary cell wall layers. The lumen is the open center of the cell. The total cell wall thickness is largely controlled by the thickness of the S2 layer. The cell wall layers are distinguished from each other by different orientation of the cellulose microfibrils in each layer. This orientation is random in the primary wall, at an angle of 50-70^{o} in the S1 layer, 10-20^{o} in the S2 layer, and 60-90^{o} in the S3 layer. The primary wall contains about 10% cellulose, increasing to more than 50% in the S2 layer, and decreasing slightly in the S3 layer. Lignin is about 70% of the middle lamella and the primary wall, about 22% in the S2 layer, and about 15% in S3. The hemicellulose fraction varies about the same as cellulose across the wall. (Thomas, 1977)

The wood structure also varies considerably across the tree. New wood, or sapwood, is produced in the

growing center (cambium) between the existing wood and the bark. As this lighter colored wood is formed, interior sapwood adjacent to the (usually) darker-colored heartwood is converted to heartwood. This occurs when the parenchyma cells which form the wood rays change their metabolic activity and produce extractives from stored carbohydrates. They then die, and the extractives diffuse into adjacent cells. Thus the heartwood generally contains no living cells, and its dark color is due to the presence of extractives. Growth rings in trees occur due to the different kinds of cells produced early or late in the growing season. In softwoods, springwood cells tend to have a large cross-sectional area with thin walls and a large open center. Summerwood cells are smaller with thicker walls and smaller centers. In hardwoods the observable differences are due primarily to the difference in vessel sizes, which are, in ring-porous hardwoods, considerably larger in the springwood than in the summerwood. In other hardwoods, termed diffuse-porous, the vessels are essentially the same size throughout the growing season and rings are difficult to distinguish.

Another important component of wood is water. In green wood, the cell walls are saturated with water and the cell cavities may be partially or completely filled with water. Green wood is generally about 50% water by weight.

Seasoned wood has the cell cavities essentially empty, with moisture present primarily in the cell walls in an amount depending on the relative humidity and the temperature. Moisture content varies from 0 at 0% relative humidity, 10% at 50% relative humidity and a temperature of 50°F, to 35% at 100% relative humidity and 50°F. Moisture content is lower at lower temperatures, for the same relative humidity. The removal of the water in the cell cavities generally has no effect on most wood properties, but removal of the cell-wall moisture has a profound effect. The dividing value is called the fiber-saturation point, and is generally between 25 and 35% moisture.

At low relative humidities, the adsorption of water by wood is due to interaction of the water with accessible hydroxyl groups on the lignin and on the non-crystalline carbohydrate regions. The differential heat of adsorption in this region is about 260 cal/g water. At high relative humidities, adsorption is believed to be due to a tendency for lignin and cellulose to disperse themselves, and the differential heat of adsorption is much smaller. (Tarkow et al, 1963)

This brief overview of wood structure indicates the complexities to be dealt with in modeling wood hydrolysis. The next section will discuss acid hydrolysis and enzymatic hydrolysis, and the types of kinetic models that have been utilized.

IV. SACCHARIFICATION KINETICS

As can be seen from the discussion of wood structure, saccharification of wood is a complex matter. It has been determined that wood is hydrolyzed more slowly than cellulose, and that the hemicellulosic portion of the wood is hydrolyzed much more easily than the cellulosic portion. In cellulose itself, amorphous cellulose is hydrolyzed much more readily than highly crystalline cellulose.

In this section the acid hydrolysis of glucose oligomers of various sizes and of cellulose will be discussed first, followed by a discussion of the acid hydrolysis of hemicellulose, especially xylans. Next acid hydrolysis of wood will be discussed, and then the solvolysis of glycosyl halides. Finally a brief discussion of enzymatic hydrolysis will be presented.

A. ACID HYDROLYSIS

1. Cellulose

The rate of hydrolysis of cellulose in concentrated acid at low temperature was studied by Freudenberg and others in the early 1930's using fuming hydrochloric acid (41-45%) or 50% or stronger sulfuric acid. It was found that cellulose was hydrolyzed more slowly than cellobiose, with cellotriose and cellotetraose lying, in that order, between cellobiose and cellulose. First order rate constants for cellulose of 0.36×10^{-4} (units not given - presumably sec^{-1}) and cellobiose of 1.07×10^{-4} were given for hydrolysis with 50% sulfuric acid at $18^{o}C$. Corresponding activation energies of 29.8 kcal and 27.3 kcal were given. For starch, the rate at $18^{o}C$ was 0.97×10^{-4} with an activation energy of 28.9 kcal. The investigators interpreted the decrease in rate with increasing chain-length as due to an increase in activation energy for the central groups compared to the terminal groups. The course of reaction was believed to be first dissolution of the cellulose, followed by hydrolysis. Increasing the acid concentration to 65% greatly increased the rate of hydrolysis. (Freudenberg, 1938; E. Harris, 1949, 1952; J. Harris, 1975)

Wolfrom and others studied the hydrolysis of cellulose

in fuming hydrochloric acid and of oligosaccharides in 51% H_2SO_4 (Wolfrom and Georges, 1937; Wolfrom and Dacons, 1952). Neither of these groups appear to have considered the formation of reversion sugar oligomers which occurs in concentrated acid solution. According to Meller (1963) this recombination is not significant with 51% sulfuric acid at the temperatures studied, but is marked with 60% and 71% sulfuric acid.

Other investigators studied cellulose hydrolysis in 85% phosphoric acid, which reacts more slowly than concentrated sulfuric or hydrochloric acid. The reaction rate was found to be first order between 12^{o} and $40^{o}C$, and independent of degree of polymerization between 130 and 1500 (Harris, 1952).

Feather and Harris used cellotriose labeled with ^{14}C to follow the progress of hydrolysis and found that the glycosidic bond at the nonreducing end of the molecule is hydrolyzed at a rate 50% higher than the one at the reducing end (Feather and Harris, 1967; J. Harris, 1975; Meller, 1969), a result which is also predicted from theoretical considerations (BeMiller, 1967). This is the case for hydrolysis in both 50% and 5% sulfuric acid. Both rate constants are significantly smaller than that for cellobiose at the same conditions (Feather and Harris, 1967; Meller, 1970), with cellobiose being hydrolyzed 1.4 times

faster than the glucosidic bond at the nonreducing end of the cellotriose molecule (Meller, 1970).

In accord with this demonstration of the relative hydrolysis rates of the glucosidic linkages being the same in 50% and in 5% sulfuric acid, it seems to be generally accepted that the mechanism of hydrolysis is the same in dilute and in concentrated acid hydrolysis. The reaction rate varies linearly with the Hammett acidity function, for the most part, though there is some deviation and the rate is different for different acids at the same Hammett acidity (Meller, 1963; Moiseev et al, 1976a; Timell, 1964). We will proceed, therefore, with an exploration of the mechanism of acid hydrolysis, and then examine some of the rate information for hydrolysis in dilute acid, which has been more extensively studied than concentrated acid hydrolysis.

Hydrolysis of cellulose proceeds through fission of the glycosyl-oxygen bond. It is generally agreed that the initial step is protonation of one of the hemiacetal-oxygen atoms to form a conjugate acid. Depending on which oxygen atom is protonated, the resulting ion can be cyclic (from protonation of the glycosidic oxygen leading to elimination of the aglycon by fission of the C-1 to exocyclic O bond) or acyclic (from protonation of the ring oxygen resulting in ring opening). There has been a considerable amount of

debate over which mechanism operates or whether both do, with most recent writing supporting the cyclic view. Harris states that due to the structured nature of water, both oxygens will be partially protonated, so the conjugate acid of both mechanisms will be the same, and the position of bond cleavage will depend on the electron-density distribution in the ring (Harris, 1975). The rate-controlling step is the formation of the conjugate acid from the protonated intermediate by an A-1 mechanism (Overend, 1972). Overend and others support the cyclic carbonium-ion intermediate hypothesis (BeMiller, 1967; Capon, 1969; Overend, 1972), which is illustrated in Figure 1.

The cyclic carbonium ion intermediate mechanism predicts the faster hydrolysis of the linkage at the nonreducing end of the molecule. This is due to the cyclic carbonium ion existing in the half-chair conformation, which would require extensive reorientation of an entire chain if it occurred at an internal linkage or at the reducing end. The solvolysis of glycosyl halides is also believed to involve the formation of a cyclic carbonium ion. Some researchers have suggested that the hydrolysis of terminal linkages is more dependent on the concentration of acid than is the hydrolysis of nonterminal linkages. They feel this explains the finding that sugar solutions of the same total reducing power contain both more low

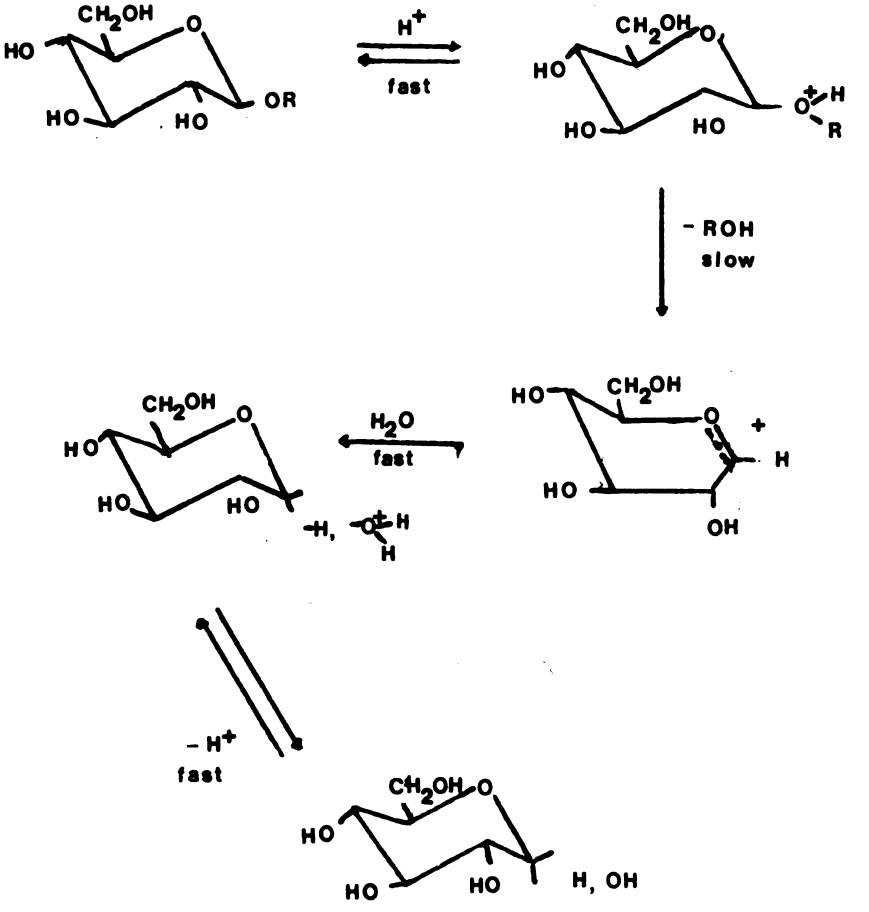


FIGURE 1

ACID HYDROLYSIS OF GLUCANS - CYCLIC MECHANISM

molecular weight and more high molecular weight products when produced by concentrated acid hydrolysis than when obtained by hydrolysis with more dilute acid (BeMiller, 1967; Moiseev, 1976a, 1976b).

A considerable amount of research has been done on the effects of ring substituents on hydrolysis of sugar glycosides. This work has been reviewed by several investigators (BeMiller, 1967; Capon, 1969; Feather and Harris, 1965, Overend, 1972).

Just as hydrolysis of sugars in concentrated acid is complicated by the formation of sugar oligomer reversion products, hydrolysis of sugars in dilute acid is complicated by the formation of sugar degradation products. This process is generally modeled as consecutive first-order reactions. Much of the research on dilute acid hydrolysis of biomass has been directed toward exploration of the relationship between the two rate constants and the use of this information to maximize the production of sugar. A more difficult complication is that in dilute acid the cellulose is not dissolved, so the reaction occurs heterogeneously rather than homogeneously. There is a rapid degradation of the amorphous fraction of the cellulose followed by a much slower hydrolysis (approximately 100 times as slow) of the crystalline regions. At the high temperatures and pressures utilized for biomass

saccharification with dilute acid, the initial reaction in the amorphous regions is so fast that it is modeled as occurring instantaneously. It has been suggested in addition that the amount of intermolecular hydrogen bonding is greater for concentrated cellulose solutions than for dilute solutions, and that this decreases the hydrolysis rate even in homogeneous reactions. Another interpretation of those experimental results was that dissolution was not complete in the more concentrated case. (BeMiller, 1965; Saeman, 1945; Sharples, 1971)

Saeman (1945) did an extensive study of glucose decomposition as a function of acid composition and temperature, obtaining an activation energy of about 33 kcal. A functional relationship between acid concentration and the rate constant was developed for sulfuric acid concentration between 0.4 and 1.6% and a temperature range of 170-190^{o}C.

2. Hemicellulose

Hemicellulose is much more easily hydrolyzed than is cellulose. This is generally attributed to two factors. One, and probably the most important in softwoods, is the difference in physical structure. Hemicellulose is much less crystalline and hence much more accessible to hydrolyzing agents. The other factor, in hardwoods, is that the linkages between the xylan units themselves are more easily hydrolyzed (about seven times as fast) than those between glucans. (Capon, 1969; Kamiyama, 1979; Timell, 1964)

The reaction mechanism appears to be the same for cellulose and hemicellulose, and it is reported that one terminal linkage is hydrolyzed at a rate 1.8 times faster than that of the internal linkages and the other terminal linkage (Kamiyama, 1979). Similarly, xylose is much more easily decomposed than glucose, giving furfural as the primary decomposition product (Harris, 1949). This reaction has been determined to be first order, with an activation energy of about 32 kcal in 0.5 to 16% sulfuric acid and a temperature of 100-200^{o}C (Root, 1959).

Under conditions used for wood hydrolysis, there is an initial period of rapid hemicellulose removal, followed by a much decreased rate. The reasons for this are not well understood (Harris, 1975). It has also been established

that softwood mannans are more resistant to hydrolysis than hardwood xylans, and xylans with a high uronic acid content are more resistant than those with a lower content (Harris, 1975).

3. Wood

Research on the kinetics of wood hydrolysis has been intimately connected to the efforts to use wood as a source of sugars and ultimately of ethanol for fuel.

The difference in hydrolysis rate between hemicellulose and cellulose has been employed to separate these two portions of the wood. This is essential in dilute acid hydrolysis processes because of the large amount of furfural and other degradation products which are formed if the hemicellulose is subjected to the harsh conditions required for hydrolysis of the cellulose. These then seriously contaminate the product sugar solutions, and furfural in particular is a strong inhibitor of fermentation.

Hydrolysis of cellulose in dilute acid is always a heterogeneous process, with a rate reported to be 1-2 orders of magnitude less than that of glycosides (Harris, 1975). Typically weight loss-vs-time curves are used, showing the rapid removal of an initial amount of material (believed to be the amorphous fraction), followed by the slow first order reaction of the remaining material from about 90% to 3% residue. No satisfactory reaction mechanism has been developed to fit this data. Random cleavage of glycosidic bonds will not give the linear (on a semilog plot) relationship which is found. Models suggesting that only the

crystalline surface is available for reaction give a poorer fit to the data than does the simple first-order model. Harris suggests that the resistance to hydrolysis is due to the rigidity of the rings in the crystalline structure.

Saeman (1945) was one of the primary investigators of the dilute sulfuric acid hydrolysis of wood. He successfully modeled the reaction as consecutive first order reactions,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where A is cellulose, B is glucose, and C is glucose degradation products. The hydrolysis rate constant, k_1, was expressed as

$$k_1 = HC_s^{\,M}\, e^{-H_a/RT}$$

where H and M are empirical constants, C_s is the sulfuric acid concentration in percent, and H_a is the activation energy. Since the rates of hydrolysis did not change as the reaction progressed, it was assumed that high molecular weight cellulose was first rapidly converted to a lower molecular weight material with a DP of about 150, which then in the rate-limiting step was slowly converted to soluble products, followed by rapid conversion to D-glucose in a step which was not rate-limiting. (E. Harris, 1949, 1952; J. Harris, 1975; Saeman, 1945)

The activation energy for the hydrolysis was found to

be 40-44 kcal, depending on the (dilute) acid used, compared to about 28 kcal for hydrolysis of cellulose in concentrated acid. Slight variations between wood species were also found. Cellulose from cotton linters and from paper have been shown to follow the same equation but with different rate constants (Fagan, 1971).

4. HF and Glycosyl Halides

In comparing HF saccharification with concentrated acid hydrolysis, it is important to note that the reaction of HF with cellulose is not a hydrolysis (Defaye et al, 1983). In fact, dry hydrogen chloride gas has no effect on cellulose (Nevell, 1976), while dry hydrogen fluoride does react with cellulose to produce glycosyl fluoride. It is therefore to be expected that significant differences may be found between the kinetics and reaction mechanism of HF saccharification and the hydrolysis mechanisms discussed in this section. Nonetheless, the starting material is the same, and many of the complications encountered in studying the reaction are the same.

We will now briefly examine some of the information about the hydrolysis of sugar halides, as this may also provide us with some insight into HF saccharification.

The solvolysis of glycosyl halides is believed to involve an S_N1 mechanism which proceeds through a cyclic carbonium ion intermediate, giving almost complete inversion of the products (Barnett, 1969; BeMiller, 1967; Capon, 1969).

The kinetics in dilute perchloric acid has been shown to be pseudo-first-order with a dependence on the Hammett acidity function and a positive entropy of activation, which suggests an A1 mechanism. Relative rates of hydrolysis

follow patterns similar to those for hydrolysis of sugar oligomers, suggesting the same cyclic carbonium-ion intermediate. β-D-glucopyranosyl fluoride is an exception, where the entropy of activation is negative and an intramolecular A2 mechanism may be involved. Free sugars were found to be the only products of hydrolysis. (Barnett, 1969; BeMiller, 1967; Capon, 1969)

It can be seen then, that the kinetics and mechanism of the solvolysis of glycosyl fluorides are quite similar to those of the acid hydrolysis of oligosaccharides. If the mechanism proposed by Defaye and his coworkers (1983) is correct, the HF saccharification of cellulose will also be similar.

B. ENZYMATIC HYDROLYSIS

The kinetics of enzymatic hydrolysis of cellulose will be described only briefly, as the kinetics of HF saccharification is likely to be much more closely related to that of acid hydrolysis than enzymatic hydrolysis.

Enzymatic hydrolysis of cellulose is the result of a specific enzyme-catalyzed reaction. Therefore sugar reversion and sugar degradation are not encountered and so do not complicate the reaction analysis. On the other hand, enzymes are much larger than acid molecules and therefore mass transfer limitations play a much more significant role. Especially in heterogeneous reactions with lignocellulosic materials, much of the cellulose polymer is unavailable to the enzyme. Also, cellulase contains more than one component enzyme, and these components will be present in different ratios depending on the source of the cellulase.

In their recent review, Lee, Fan and Fan (1980) summarize the important factors in the enzymatic hydrolysis of insoluble cellulose as (1) the structural features of the cellulose, (2) the nature of the enzyme system employed, and (3) the mode of interaction between the cellulose and the enzyme. They conclude that a kinetic model incorporating all three factors has not yet been proposed.

Most kinetic studies of enzymatic hydrolysis have

dealt with soluble substrates. The simplest is the hydrolysis of cellobiose by cellobiase. It was found that cellobiase from T. viride contains three separate but similar fractions which hydrolyze cellobiose in accordance with the same rate expression but with different rate constants (Lee et al, 1980). Non-competitive product inhibition by glucose is found. Studies of enzymatic hydrolysis of β-1-4 oligoglucosides with DP up to 6 found the reaction to be inhibited by an increase in concentration of the substrate as well.

When the heterogeneous system is considered, the diffusion of the enzymes into the structural matrix of the cellulose and adsorption and desorption of the enzymes must be considered. Adsorption has been found to be largely independent of pH but strongly dependent on temperature and on the type of cellulose present. The influence of cellulose type may be related to the amount of available surface area, as diffusion of enzyme into cellulose particles is usually negligible because the enzyme molecule is larger than most of the cellulose pores. The amount of available surface area is further affected by fragmentation of the cellulose particles during the course of the reaction. Evidence that the reaction slows down after a certain time period even though the amount of available surface is still large is the basis for the

suggestion that the surface area is composed of two fractions, active and inactive, and the rate of hydrolysis may be dependent on the amount of active surface area present.

Cellobiose has been shown to cause significant competitive inhibition of the reaction. Glucose causes a milder inhibition. It has been reported that the inhibitory effect of products varies with the organism from which the cellulase is derived.

The model most commonly used for the kinetics of heterogeneous enzymatic catalysis is the Michaelis-Menten mechanism in various modified forms. Some of the more advanced models are a combination of enzyme adsorption equations with Michaelis-Menten kinetics. Other models have attempted to incorporate the presence of different cellulase components which react differently on molecules of varying DP. Other models have incorporated diffusion into the Michaelis-Menten kinetics, but none so far has successfully incorporated all the features known to affect the reaction. (Lee et al, 1980; Nisizawa, 1973)

V. MODELING OF HF SACCHARIFICATION

The modeling of HF saccharification of lignocellulosic materials must begin with the physical and chemical structure of the substrate. As we discussed earlier, this research has focused on poplar as a substrate, since it would be a likely candidate for the feedstock for a commercially viable HF saccharification process. We discussed typical structure of a hardwood tree in Section III, and now we will formulate a model of how HF might react with that wood.

The usual harvesting method for an energy plantation is whole-tree chipping, so we will assume our feedstock is standard sized wood chips. Because we have not investigated the reaction of HF with bark, we will simplify the model by assuming bark-free chips, and we will further assume that the chips have been dried to an acceptable moisture level.

Acceptable water content for the wood chips is an optimization problem involving several factors. In order to avoid an azeotrope-breaking step in the HF recycle stream (HF and water form an azeotrope at 38% HF by weight) it would be desirable to have going into the reaction system with the wood only the amount of water taken up in the

reaction. If the reaction produces a 100% yield of monomeric sugars, this amounts to wood containing 8.44% water by weight. However the product distribution of monomeric and oligomeric sugars depends on the water concentration of the HF and on the method of HF removal, so the actual amount of water reacting will be a fairly complex function of other process conditions. Ultimately the range of acceptable water concentrations will be determined by the relative economics of HF:wood operating ratio, cost of water removal from the HF, and cost of wood drying.

When the chips are contacted with liquid HF, several steps occur. First is reaction of the exposed cellulose and hemicellulose on the surface of the chip with the HF. The hemicellulose reacts more quickly than the cellulose, and amorphous regions of the cellulose more quickly than the highly crystalline regions. This reaction itself is complex. HF forms hydrogen bonds with the cellulose and breaks the hydrogen bonds between cellulose molecules and the intramolecular hydrogen bonds that impart rigidity to the cellulose molecules, resulting in the dissolving of the cellulose in the hydrogen fluoride. It also breaks the glycosidic linkages between the glucan or xylan units, producing glycosyl fluorides. These sugar fluorides react with water, producing free sugars and HF. Sugars also recombine, in the presence of HF, forming sugar oligomers

of various sizes. As a result, the composition of the liquid fraction changes with time.

At the liquid-solid interface HF molecules diffuse towards the surface and cellulose molecules and glycosyl fluorides diffuse away from the surface. The direction of the diffusion of water depends on the relative concentrations of water in the HF solution and in the wood, as well as in which phase and how fast reaction of the glycosyl fluorides with water occurs.

The particle size and the geometry of the surface change with time, as does its composition. A fresh uniform wood surface is first depleted of hemicellulose, next of amorphous cellulose, and finally of crystalline cellulose, with a consequent enrichment in the fraction of lignin it contains.

In addition to this reaction on the surface, HF penetrates into the pores of the wood, which account for about 55% of its volume. The HF molecule is smaller than a water molecule, so is capable of diffusing through the wood pore system. All the reactions which occur on the surface, then, also occur inside the wood particles in the pores. However, the sugar, glycosyl fluorides, sugar oligomers, and dissolved cellulose produced have much more difficulty diffusing out of the wood chip than the HF does diffusing in, since they are much larger in size. It should also be

recalled that the pores run parallel to the fibers, so diffusion of HF into the wood chips occurs in this direction preferentially and is therefore anisotropic. Again, the reaction of HF with cellulose and hemicellulose in the pores changes the geometry of the pores with time, just as occurs on the particle surface. Finally, some combination of diffusion and reaction into the particle through the surface and through the pore walls also occurs. The pits in the fiber and pore walls which allow the passage of sap also allow the passage of HF, especially when further thinned and enlarged by HF reaction.

Thus what we have, if we consider just one wood chip, is a particle whose geometry and composition change with time both internally and externally. Its surface shrinks and it becomes more porous as hemicellulose and cellulose are removed, leaving the lignin matrix. If the particle is undisturbed, this lignin matrix retains the shape of the wood chip, though softer, somewhat swollen, and much more flexible (Clark, 1962; Luers, 1938). If the reaction mixture is stirred, the lignin matrix eventually disintegrates into a fine powder. During the course of the reaction, concentration gradients appear, with HF diffusing towards and into the chip, and sugars, sugar fluorides, and cellulose molecules of varying lenghts diffusing out of and away from the ship, causing a complex pattern of mass

transfer resistances external to and within the particle. Diffusion within the chip is both along the pores and into the cell walls, with probably very different characteristics in the different directions. To further complicate the situation, the solid portion of the wood particle is not uniform in composition. As discussed in Section III, the compound middle lamella between the cells is about 70% lignin, which is not soluble in HF and appears not to react strongly with it, and therefore would be capable to some extent of protecting the cellulose it surrounds from attack by the HF. Lignin concentration and hence presumably its protecting power decreases in the secondary cell wall, with a corresponding increase in cellulose and hemicellulose content. Thus the resistance of the solid to HF saccharification depends on whether that solid is lamella or cell wall, and even on what portion of the cell wall it is.

If the model is not already complex enough, other important factors remain to be considered. First, the size of the wood pores is not uniform, and there are significant seasonal variations in many species, with springwood pores being considerably larger than summerwood pores. Second, the size of the wood chips themselves is not uniform, so a distribution of original particle sizes must be considered. In addition, we have not discussed the effect

of ash and extractives on the reaction rate. Indeed, their effects, if any, are unknown.

Further complexities are found on the molecular level. Cellulose, as discussed in Section III, consists of thread-like chains of glucose residues joined by β-1-4 glycosidic linkages, with molecular weight greater than 100,000. As mentioned earlier, different regions of cellulose vary in crystallinity, with amorphous cellulose being more easily hydrolyzed than crystalline cellulose. It is possible for regions within a single cellulose molecule to vary in crystallinity also, with a resultant increase in reaction rate expected for the portions of the molecule with a higher degree of disorder. Further, if Defaye and his coworkers (1983) are correct in postulating that the reaction of cellulose and HF occurs by protonation and formation of the conjugate acid followed by formation of the oxocarbonium ion as occurs in acid hydrolysis, the same difference in reactivity of reducing end and internal linkages vs. non-reducing end linkages would be expected, since the rate-determining step, the formation of the oxocarbonium ion, is likely to be the same. The reaction of solubilized cellulose would then proceed by random bond splitting plus an additional increment of monomer formation from the preferential reaction at the non-reducing end of the molecule. This would lead to an apparent increase in

reaction rate with time as the random bond-breaking increased the number of molecules and hence the number of non-reducing ends. As was discussed in Section IV, this approach has not been helpful in analyzing reaction data for wood hydrolysis, as the data fit was actually inferior to that from a simple first-order expression.

The multiple reactions involved must also be considered. In concentrated HF solution, reversion of sugars to sugar oligomers is a very significant reaction and cannot be ignored. The reaction of sugar fluorides with water to form monomeric sugars and HF is also an important reaction to be considered. Fortunately no significant sugar degradation, either of hexoses or pentoses, occurs under the reaction conditions studied, so these reactions do not need to be included.

The presence of lignin and its action as a protective shield around the cellulose has already been mentioned. In addition, the lignin matrix increases the rigidity of the cellulose molecules. The combination of these factors leads to a 1-2 order of magnitude decrease in the reaction rate of wood as compared to cellulose for acid hydrolysis (see Section IV) and is likely to have a similar effect in HF saccharification. As discussed in Section III, it is now generally accepted that covalent bonds occur to some extent between the lignin and the hemicellulose. Their

effect on reaction rates is not known. It has also been suggested that sugar-lignin adducts can be formed during acid hydrolysis (Linn, 1957), especially from the xylans.

Another type of complication is the determination of what the reaction products of interest are, and how they are to be measured. Experiments with dilute acid have generally looked at two quantities - cellulose weight loss and quantity of sugar monomers produced - as a function of time and reaction conditions. Studies in concentrated acid looked at specific rotation, reducing power, and viscosity as measures of reaction. The formation of reversion products can lead to considerable error with these measurements of the extent of reaction (Freudenberg, 1938; E. Harris, 1949, 1952; J. Harris, 1975; Meller, 1963; Wolfrom and Dacons, 1952; Wolfrom and Georges, 1937). Production of water-soluble sugars is another measurement and the one we have primarily employed, even though unreacted cellulose oligomers which are small enough to be soluble are then considered as reaction products just as are reversion oligomers, a view which obviously is not completely accurate. It should also be noted that a molecule of soluble sugar oligomer might contain <u>both</u> unreacted cellulosic β-1-4 linkages and α-linkages formed by reversion.

In spite of all these complications, it was possible for acid hydrolysis to be modeled with wood and with cellulose

as (at least pseudo-) first order reactions, and then to explore the dependence of the kinetic parameters on the Hammett acidity, acid type, cellulose type, wood species, etc., all of which were found to affect the reaction. We propose here to present a simplified model of the reaction of HF with a wood chip and then to utilize this model in developing kinetic parameters for HF saccharification.

We now consider the reaction of one standard-sized wood chip with an excess of liquid hydrogen fluoride. The physical structure of the wood was discussed in Section III. In brief, the wood chip will have dimensions of about 3 cm x 3 cm x 0.5 cm. The major structural components are fibers and pores which run in the longitudinal direction. In this tree the pores have an inner diameter averaging 25 μm and the fibers an inner diameter averaging 10 μm (Anderson, 1979; Boyd, 1979). The cell walls are relatively impermeable so the passage of fluid between pores and fibers occurs primarily through the numerous pits in the cell walls. The pores are connected to each other longitudinally by perforation plates which cause very little resistance to flow. The vessels formed by the connected pores can be as much as 3 m in length. Therefore in the longitudinal direction flow is primarily through the connected pores, which act essentially as straight channels through the chip. In the transverse direction the flow

is through a complex network of smaller diameter pits and cell interiors. This structure causes a 3-6 order of magnitude difference in permeability of wood to air in the longitudinal and transverse directions (SERI, 1979). The total void volume is about 55% of the wood.

The average chemical composition of our tree species is:

50% cellulose
29% hemicellulose
16.6% lignin
4.1% extractives
0.3% ash

The cellulose is essentially pure glucan ($C_6H_{10}O_5$). The hemicellulose is about 75% xylan ($C_5H_8O_4$) and 20% glucan, with small amounts of mannan and other sugars comprising the remaining 5%. Lignin is a complex molecule based primarily on the phenylpropane unit, and has a composition of about 59.8% carbon, 6.4% hydrogen, and 33.7% oxygen by weight. The extractives are composed of a large variety of substances, as was discussed in Section III. The ash composition of our tree is, after oxidation, 49% CaO, 8% K_2O, 7% MgO, 4% SiO_2, 2% P_2O_5, 1% Fe_2O_3, 25% CO_2, and the remaining 3% Na_2O, TiO_2, Al_2O_3 and SO_3.

What we need, however, is the chemical composition in terms of total glucan, xylan, mannan, etc. Unfortunately,

all existing standard analysis techniques for the determination of sugar in wood suffer from some degree of incomplete hydrolysis and sugar degradation, making accurate quantitative sugar analysis very difficult (Fengel, 1979). We have therefore used our experimental determination of maximum sugar yields from the wood of our experimental tree (reinforced by our quantitative yield from filter paper) to estimate the sugar concentration in the unreacted wood chips as

3.441×10^{-3} moles glucan/g wood

(0.557 g glucan/g wood)

1.4×10^{-3} moles xylan/g wood

(0.185 g xylan/g wood)

and we have ignored the remaining minor sugars. On a volumetric basis this corresponds to

$0.224\ g/cm^3$ glucan

$0.072\ g/cm^3$ xylan

$0.101\ g/cm^3$ lignin, extractives, etc.

$0.003\ g/cm^3$ ash

$0.400\ g/cm^3$ density of dry poplar

We now examine the reaction of one standard-sized wood chip with a large volume of liquid HF. We will assume that the HF immediately fills all the void spaces in the wood, and reaction commences.

The lignin and extractive fraction will be considered

essentially inert to HF, and the undisturbed lignin framework will preserve the size and structure of the chip throughout the reaction (Clark, 1962; Luers, 1938).

The ash will react with HF to form fluoride salts, which will generally be soluble in the liquid hydrogen fluoride but insoluble in water except for the potassium fluoride. Because of the very small amount of ash present and the large excess of HF, this reaction will be insignificant and we shall not consider it further.

The cellulose and hemicellulose can undergo two different types of reaction with HF. First, HF can break the hydrogen bonds between adjacent cellulose and/or hemicellulose molecules and between these molecules and the lignin and dissolve the cellulose and hemicellulose. This can be written as

(a) $$H\text{-}(C_6H_{10}O_5)_n\text{-}OH \xrightarrow{HF} H\text{-}(C_6H_{10}O_5)_n\text{-}\dot{O}H$$

solid in HF solution

with a similar reaction for hemicellulose.

Alternatively or concurrently HF can cleave the covalent bonds between sugar residues, resulting in the formation of molecules of a lower DP and sugar fluorides. This reaction with solid cellulose can be written as

(b) $H\text{-}(C_6H_{10}O_5)_n\text{-}OH \xrightarrow{HF} H\text{-}(C_6H_{10}O_5)_j\text{-}F + H\text{-}(C_6H_{10}O_5)_k\text{-}OH$

solid solid solid

followed by

(a') $H\text{-}(C_6H_{10}O_5)_j\text{-}F \xrightarrow{HF} H\text{-}(C_6H_{10}O_5)_j\text{-}F$

solid in HF solution

or with dissolved cellulose as

(b') same as (b) but all components in solution

where $j + k = n$, and again analogous reactions occur with hemicellulose except that covalent bonds between hemicellulose and lignin may also be cleaved.

These sugar fluorides can then react with water to produce sugar oligomers and release HF:

(c) $H\text{-}(C_6H_{10}O_5)_j\text{-}F + H_2O \longrightarrow H\text{-}(C_6H_{10}O_5)_j\text{-}OH + HF$

solid solid

and

(c') same as (c) but in solution

with again analogous reactions for hemicellulose.

In addition, in acid solution glucose and xylose recombine to form oligomeric reversion products which are primarily α-1-6 linked, as opposed to the β-1-4 linkages

in cellulose, so we can have

(d) $H\text{-}(C_6H_{10}O_5)_h\text{-}OH + H\text{-}(C_6H_{10}O_5)_i\text{-}OH \xrightarrow{HF}$

$$H\text{-}(C_6H_{10}O_5)_h\text{-}(C_6H_{10}O_5)_i\text{-}OH + H_2O$$

with an α-1-6 linkage between the h and i groups, with an analogous reaction for hemicellulose.

We also have a similar reaction occurring between glycosyl fluorides and sugars

(e) $H\text{-}(C_6H_{10}O_5)_h\text{-}F + H\text{-}(C_6H_{10}O_5)_i\text{-}OH \xrightarrow{HF}$

$$H\text{-}(C_6H_{10}O_5)_h\text{-}(C_6H_{10}O_5)_i\text{-}OH + HF$$

with a similar reaction for hemicellulose.

Hemicellulose is expected to react with HF much faster than cellulose in reactions of type (a), (a'), (b) or (b') by analogy with acid hydrolysis. About 20% of the hemicellulose is glucan and the rest primarily xylan. The reaction of xylan with HF in (b), (b'), (c) or (c') type reactions is expected to be considerably faster than that of glucan from either cellulose or hemicellulose. In addition, the rate of reactions (a), (a') and (b) is expected to be dependent on the crystallinity of the substrate, with reaction fastest in amorphous regions. Since (b') occurs in solution, the original substrate crystallinity should not affect its rate. However the rates of all the reactions

above can be affected by the position in the molecule of the bond being broken and the bond linkage type.

As can be seen from the above, we have a distribution of substrate and product molecules undergoing a variety of reactions. To simplify this reaction scheme, we will classify the various species as follows:

1 cellulosic glucan, solid, crystalline

2 cellulosic or hemicellulosic glucan, solid, amorphous

3 hemicellulosic xylan, solid, amorphous

4 glucan, soluble in HF, insoluble in water

5 xylan, soluble in HF, insoluble in water

6 glucan, soluble in both HF and water

7 xylan, soluble in both HF and water

8 HF

9 water

10 lignin, solid

We are ignoring the presence of extractives and ash, and not differentiating glucosyl and xylosyl fluorides from glucans and xylans. The reaction products we measure are species 6 and 7. The reactions of interest will be

$1 \xrightarrow{HF} 4$ solid crystalline glucan → HF-soluble glucan

$1 \xrightarrow{HF} 6$ solid crystalline glucan → water-soluble glucan

$2 \xrightarrow{HF} 4$ solid amorphous glucan → HF-soluble glucan

$2 \xrightarrow{HF} 6$ solid amorphous glucan → water-soluble glucan

$3 \xrightarrow{HF} 5$ solid xylan → HF-soluble xylan

$3 \xrightarrow{HF} 7$ solid xylan → water-soluble xylan

in the solid phase, and

$4 \xrightarrow{HF} 6$ HF-soluble glucan → water-soluble glucan

$5 \xrightarrow{HF} 7$ HF-soluble xylan → water-soluble xylan

in the liquid phase. Other reactions, such as reaction of water-soluble glucan with HF to produce glucans of lower DP and recombination of glucans to produce reversion glucans of larger DP will not be considered.

In our modeling of the batch reaction of excess HF with one wood chip, we will further assume that we have a perfectly mixed bulk liquid phase with a film resistance between the bulk liquid and the liquid-filled wood chip, that the volume of the bulk liquid phase is constant, that the initial concentration of all species is uniform throughout the wood chip, that the resistance for transfer between phases is uniform over the chip surface, and that at any time, the concentration of all species is uniform over the surface. Further, we will deal with the porosity of the solid implicitly rather than explicitly by considering it as pseudo-homogeneous with a much larger effective diffusivity in the longitudinal (y) direction than in the transverse (x and z) directions. The coordinate system

and the chip dimensions are shown in Figure 2. Notation is shown in Table 1 and initial and boundary conditions in Table 2.

Then a mass balance on the bulk liquid phase from time t to t+Δt will give

$$(f) \quad V_b C_{ib}|_{t+\Delta t} - V_b C_{ib}|_t = n_i S \Delta t + r_i^{\ell} V_b \Delta t \qquad i=1\text{-}10$$

and the balance for transfer between phases will be

$$(g) \qquad n_i = k_i (C_{ib} - C_{is})$$

where k_i will be an effective mass transfer coefficient incorporating transfer due to reaction in the film thickness.

Combining these equations and taking the limit as $\Delta t \to 0$ gives

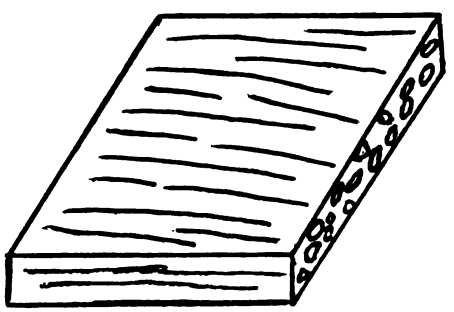
$$(h) \qquad \frac{dC_{ib}}{dt} = \frac{Sk_i}{V_b} (C_{ib} - C_{is}) + r_i^{\ell}$$

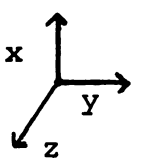
Simplifying, we can use equation (h) for species 4-9 and specify

$$C_{ib} = 0 \qquad i = 1,2,3,10$$

for any time t.

A mass balance on the solid phase and the fluid it contains in its voids will require a differential solid





x from -T/2 to T/2

y from -L/2 to L/2

z from -W/2 to W/2

$W \simeq L \simeq 3$ cm

$T \simeq 0.5$ cm $\simeq W/6$

FIGURE 2

WOOD CHIP

TABLE 1

NOTATION

V_b = volume of bulk liquid phase cm^3

C_i = concentration of species i inside particle, based on liquid volume for soluble species, on particle volume for insoluble species g/cm^3

C_{is} = concentration of species i on particle surface g/cm^3

C_{ib} = concentration of species i in bulk liquid g/cm^3

S = surface area of chip cm^2

ρ_w = density of wood (at initial conditions) = 0.4 g/cm^3

ρ_{HF} = density of HF = 0.96 g/cm^3

n_i = mass flux of species i from solid surface $g/cm^2 sec$

r_i^{ℓ} = mass rate of production of species i based on liquid volume - used for soluble species

r_i^{s} = mass rate of production of species i based on particle volume - used for insoluble species

ε = void fraction of wood (= 0.55 at initial conditions)

D_{ij} = effective diffusivity of species i in the j direction, based on total particle area normal to flow (ie not on pore area alone)

k_i = effective mass transfer coefficient for species i

TABLE 2

INITIAL CONDITIONS

$$C_1^i + C_2^i = 0.224 \text{ g/cm}^3$$

$$C_3^i = 0.072 \text{ g/cm}^3$$

$$C_4^i = C_5^i = C_6^i = C_7^i = 0$$

$$C_{10}^i = 0.104 \text{ g/cm}^3$$

$$C_{jb}^i = 0 \quad j = 1,\ldots,7,10$$

$$C_8^i = C_{8b}^i = \rho_{HF} - C_{9b}^i = .96 - C_{9b}^i \text{ g/cm}^3$$

$C_9^i = C_{9b}^i$ specified by experimental conditions

volume element, illustrated in Figure 3.

A mass balance on this solid element from time t to t+Δt gives

$$
\begin{aligned}
&C_i \Delta x \Delta y \Delta z\big|_{t+\Delta t} - C_i \Delta x \Delta y \Delta z\big|_t = \\
&\quad -D_{iz}\frac{\partial C_i}{\partial z}\Big|_{x,y,z} \Delta t \Delta x \Delta y + D_{iz}\frac{\partial C_i}{\partial z}\Big|_{x,y,z+\Delta z} \Delta t \Delta x \Delta y \\
&\quad -D_{iy}\frac{\partial C_i}{\partial y}\Big|_{x,y,z} \Delta t \Delta x \Delta z + D_{iy}\frac{\partial C_i}{\partial y}\Big|_{x,y+\Delta y,z} \Delta t \Delta x \Delta z \\
&\quad -D_{ix}\frac{\partial C_i}{\partial x}\Big|_{x,y,z} \Delta t \Delta y \Delta z + D_{ix}\frac{\partial C_i}{\partial x}\Big|_{x+\Delta x,y,z} \Delta t \Delta y \Delta z \\
&\quad +r_i^s \Delta x \Delta y \Delta z \Delta t + r_i^{\ell} \Delta x \Delta y \Delta z \Delta t
\end{aligned}
\tag{i}
$$

where we assume that the element is small enough that $\frac{\partial C_i}{\partial j}$ is approximately constant over k to k+Δk for k≠j and r_i^s and r_i^{ℓ} are approximately constant over the differential volume. Then we divide by Δt, Δx, Δy, and Δz and take the limit as all these quantities go to zero and get

$$
\begin{aligned}
\frac{\partial C_i}{\partial t} = &\frac{\partial}{\partial z}\left(D_{iz}\frac{\partial C_i}{\partial z}\right) + \frac{\partial}{\partial y}\left(D_{iy}\frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial x}\left(D_{ix}\frac{\partial C_i}{\partial x}\right) \\
&+ r_i^s + r_i^{\ell}
\end{aligned}
\tag{j}
$$

If we assume that D_{ij} is not a function of j, then this simplifies to

$$
\frac{\partial C_i}{\partial t} = D_{iz}\frac{\partial^2 C_i}{\partial z^2} + D_{iy}\frac{\partial^2 C_i}{\partial y^2} + D_{ix}\frac{\partial^2 C_i}{\partial x^2} + r_i^s + r_i^{\ell} \tag{k}
$$

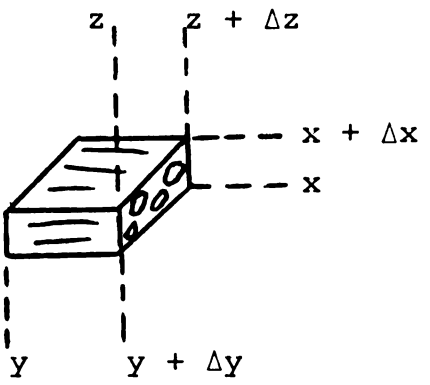


FIGURE 3

DIFFERENTIAL SOLID ELEMENT

We can further simplify this to

$$\frac{\partial C_i}{\partial t} = r_i^s \quad i = 1,2,3$$

$$(1) \qquad \frac{\partial C_i}{\partial t} = D_{iz}\frac{\partial^2 C_i}{\partial z^2} + D_{iy}\frac{\partial^2 C_i}{\partial y^2} + D_{ix}\frac{\partial^2 C_i}{\partial x^2} + r_i^{\ell} \quad i = 4\text{-}9$$

$$\frac{\partial C_{10}}{\partial t} = 0$$

Examining the relative magnitude of the diffusion terms, we recall that we assumed C_{is} is uniform. At the center of the chip C_i is some definite value. If we assume a monotonic decreasing or increasing profile, depending on the species, we have, on average

$$\frac{\partial^2 C_i}{\partial z^2} \simeq \frac{\partial^2 C_i}{\partial y^2} << \frac{\partial^2 C_i}{\partial x^2}$$

since the x dimension is much smaller than the y or z dimensions. Because of the physical properties of the wood, we have

$$D_{iy} >> D_{ix} \simeq D_{iz}$$

Therefore $D_{iz}\frac{\partial^2 C_i}{\partial z^2}$ is the product of two small terms so can be ignored, reducing the problem to two dimensions.

An alternative approach is to consider the effect of sealing off the yx faces of the chip. Because this affects

the surface area very little, we would not expect it to have much effect on the reaction rate. However sealing off the yz faces would significantly reduce mass transfer through the surface, and sealing off the xz faces would eliminate mass transfer through the pore structure, so either would significantly affect the reaction rate.

Employing this simplification reduces equation (1) to

$$\frac{\partial C_i}{\partial t} = r_i^s \qquad i = 1\text{-}3$$

$$\frac{\partial C_i}{\partial t} = D_{iy}\frac{\partial^2 C_i}{\partial y^2} + D_{ix}\frac{\partial^2 C_i}{\partial x^2} + r_i^\ell \qquad i = 4\text{-}9 \tag{m}$$

$$\frac{\partial C_{10}}{\partial t} = 0$$

Then for the two-phase system we have the equations in (m) above plus the liquid phase equations from (h)

$$\frac{dC_{ib}}{dt} = \frac{Sk_i}{V}(C_{ib} - C_{is}) + r_i^\ell \qquad i = 4\text{-}9$$

(h)

$$C_{ib} = 0 \qquad i = 1\text{-}3,10$$

It is important to recall that the reaction rates r_i will contain terms for all the reactions in which species i is involved. For example, the rate r_6^ℓ for production of water-soluble glucan will contain terms for production directly from solid amorphous cellulose, and for production

from dissolved cellulose. For a species i (solid) → j (liquid), r_i^s and r_j^ℓ will be connected by the void fraction, so

$$r_i^s = -r_j^\ell \cdot \varepsilon$$

In addition, both the effective diffusivities D_{ij} and the void fraction ε will be functions of time.

Thus in spite of the simplifications we have made, we still have a rather complex model, with many unknown parameters, including all the reaction rates, all the effective diffusivities and their time dependence, and all the mass transfer coefficients. In addition we have not considered the temperature dependence of the reaction rates, which will introduce coupled energy balance equations unless the particles and surrounding fluid can be considered isothermal.

Therefore to utilize a model of HF saccharification of wood at this stage of our knowledge, further simplifications are required. By reducing the particle size we can eliminate mass transfer and heat transfer resistance. We can then assume concentration and temperature are uniform in the solid and in the liquid, so the equations in (m) and (h) simplify to

$$\frac{dC_i}{dt} = r_i^s \qquad i = 1\text{-}3$$

$$C_{ib} = 0 \qquad i = 1\text{-}3$$

$$\frac{dC_i}{dt} = r_i^{\ell} = \frac{dC_{ib}}{dt} \qquad i = 4\text{-}9$$

$$\frac{dC_{10}}{dt} = 0 = C_{10b}$$

To simplify the reaction terms themselves, we need to simplify the reaction scheme. If we assume the reaction of crystalline and of amorphous cellulose can be represented by some average rate, and further assume the reaction sequence is

$$\text{solid cellulose} \xrightarrow{HF} \text{HF-soluble cellulose}$$
$$\xrightarrow{HF} \text{water-soluble glucan}$$

and

$$\text{solid xylan} \xrightarrow{HF} \text{HF-soluble xylan}$$
$$\xrightarrow{HF} \text{water-soluble xylan}$$

we then have a simple sequential set of reactions.

By considering the reaction of HF with filter paper, we can further simplify the reaction scheme since this will give us essentially pure crystalline cellulose reacting with hydrogen fluoride.

The reaction rate expressions themselves are expected to be functions of glucan or xylan concentration, HF concentration, and water concentration. Using a large excess of HF and of water will result in the concentrations of these two species remaining essentially constant, so that the reaction rates will be functions only of glucan and xylan concentration. The dependence on water concentration can be studied by varying the initial concentration of water in the HF.

Further discussion of these models and the experimental results are presented in the sections following.

VI. EXPERIMENTAL PROCEDURES AND DATA ANALYSIS METHODS

The reaction of wood or cellulose with HF was carried out inside a fume hood in a Kel-F vacuum distillation system manufactured by Toho Kasai Co. of Japan and marketed in the United States by Peninsula Laboratories, Inc. The reaction vessel was modified to accomodate a teflon sample line and a teflon thermal well containing a thermocouple. The wood used was Bigtooth aspen (Populus grandidentata) which had been thoroughly dried in a vacuum desiccator. Wood particle sizes investigated were 60 mesh ground wood (particles less than 0.2 mm), "small" wood chips (1-3 cm in length, 0.2-0.8 cm in width and 0.05 to 0.2 cm in thickness), and "large" or standard wood chips (2-3 cm in length and in width, and approximately 0.5 cm in thickness). Cellulose used was Whatman No. 1 filter paper cut into approximately 0.5 cm squares and dried in a vacuum disiccator. Cylinders of liquid HF were purchased from Matheson Gas Products Co.

A weighed amount of inositol (.25-.5 g, dried in a vacuum disiccator) as an internal standard was placed in the reaction vessel with a magnetic stirring bar. The weight of the reaction vessel and its contents was then determined. Next the vessel was attached to the vacuum

line and the line and vessel briefly evacuated while the vessel was cooled in liquid nitrogen. After ascertaining that there were no leaks in the system, HF was poured into the reaction vessel by opening and inverting the HF cylinder. When approximately the correct amount of HF (20-40 ml) was in the vessel, the cylinder was closed and cooling with liquid nitrogen continued to freeze the HF. The exact amount of HF present was then determined by removing the vessel from the line and reweighing it (in the fume hood). The desired amount of water (in % of the HF present) was calculated and added to the reaction vessel, which was then returned to the vacuum line. The vessel was then warmed to the desired reaction temperature and maintained at that temperature by an ice or methanol-water ice bath of appropriate composition.

When the vessel had stabilized at the desired reaction temperature, it was again briefly removed from the vacuum line, a weighed amount of dried wood or cellulose added (.2-.5 g) and the vessel returned to the line. The time of addition of the cellulose or wood was the starting time for the reaction. (Because this experimental procedure does involve opening the reaction vessel and physically adding the substrate, the temperature range studied is limited by the experimenter's tolerance for the release of fuming HF vapor into the hood, which in this case meant

temperatures under 5°C. HF boils at 19.5°C and has a vapor pressure of .48 atm at 0°C (Gall, 1980).) The system was then minimally pressurized with nitrogen or air to permit sample removal. The reaction system is shown in Figure 4.

At predetermined intervals, small (0.1-0.3 g) samples of the continously stirred reaction mixture were removed through the 0.8 mm ID teflon sample line into a teflon sample vial containing 2 or 3 ml water, which quenched the reaction by diluting the HF. Before each sample was taken, the sample line was flushed into a waste vial containing about 20 ml water. Reaction temperature was monitored via the thermocouple.

The sample mixture was neutralized with calcium carbonate, producing a calcium fluoride precipitate, water, and carbon dioxide. The mixture was then centrifuged to separate the soluble sugar reaction product from the excess calcium carbonate, calcium fluoride, lignin, residual cellulose, insoluble sugar oligomers, and any other insoluble material.

The liquid fraction was analyzed for total sugars by gas chromatography using an alditol acetate derivatization (Albersheim et al, 1967). The inositol internal standard was shown to be unaffected by the HF reaction so it could be used to control for variations in sample size and for sugar loss during neutralization and separation of the

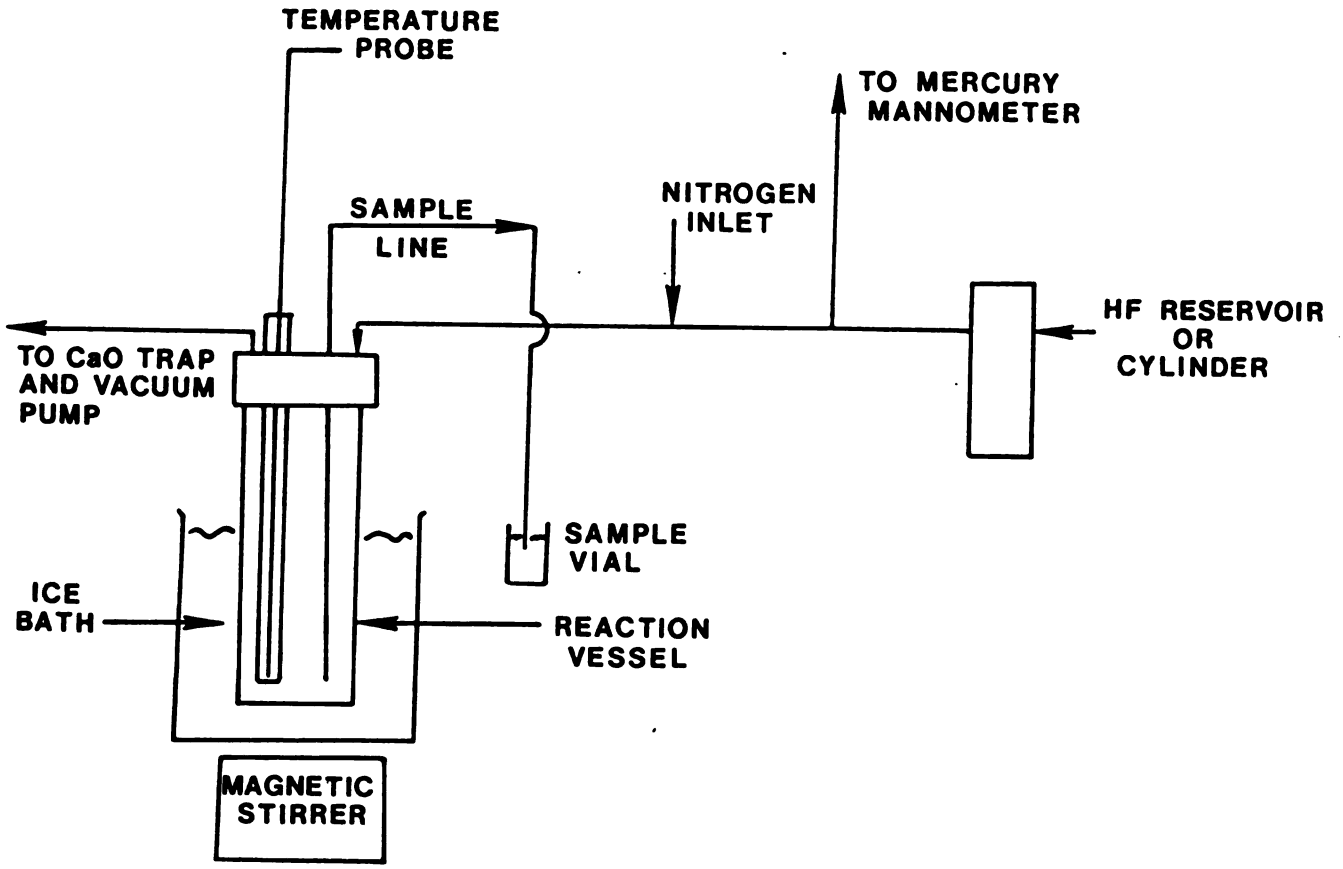


FIGURE 4

EXPERIMENTAL APPARATUS

liquid and solid fractions, as well as for the usual corrections during the derivatization procedure and GC analysis, which include hydrolysis losses, differences in GC injection sizes, and differences in detector response to the various sugars. All derivatizations and GC analyses were done in duplicate.

Studies were conducted at temperatures from -43°C to 4°C, with most of the data between -13°C and 2°C. Water concentrations investigated were anhydrous HF (as purchased from Matheson), HF with 3.6% water by weight, and HF with 6.4% water by weight. The anhydrous HF may have contained a very slight amount of water as an impurity, since it was used as purchased and not dried further.

In the data analysis, three methods were used. The first was a linear regression calculator program which minimizes the sum of the squared errors. In this analysis the reaction temperature was assumed to be constant at its average value.

The second method used was a nonlinear curvefitting program, KINFIT4, developed by James Dye and others at Michigan State University (Dye and Nicely, 1971). With this method, the temperature variation during the reaction was incorporated by treating the reaction temperature between samples as constant at the average of the readings for the two samples.

In both these cases the reaction was treated as essentially homogeneous with all water-soluble sugars regarded as reaction products, ignoring intermediates such as glycosyl fluorides (which would be hydrolyzed to glucose or xylose during the analysis procedure) and not distinguishing between water-soluble sugar oligomers formed by reversion and those formed by incomplete hydrolysis of cellulose. The reaction for cellulose

$$C + HF \overset{k}{\rightarrow} G$$

where C is cullolosic glucan and G is water-soluble glucan, was regarded as pseudo-first order. Because HF and water were present in large excess, they would not appear explicitly in the rate expression,

$$\frac{dC_C}{dt} = -kC_C \qquad C_C = \text{concentration of C}$$

or

$$C_C = C_{C_o} e^{-kt} \qquad C_{C_o} = \text{initial concentration of C}$$

and

$$C_G = C_{C_o} - C_C$$

The ratio of HF to glucan plus xylan was generally about 30 g HF to 0.5 g wood or 0.3 g cellulose, for a molar ratio of about 850 to 1. At the lowest water concentration (3.6%), the ratio of water to glucan was about 1 g water to 0.5 g wood or 0.3 g cellulose, for a molar ratio of about

30 to 1. Thus even if all glucan and xylan reacted with one molecule of HF and with one of water per monomer unit (which they do not, due to the formation of reversion oligomers), HF and water are in enough excess to be treated as constant in concentration.

For xylose a similar formulation was used:

$$H + HF \overset{k}{\rightarrow} X$$

where H is hemicellulosic xylan and X is water-soluble xylan.

The third method also used the KINFIT4 program with the temperature variation handled as above. In this case the consecutive reaction model discussed in Section V was used. As before, the end product was considered to be all water soluble sugars. The intermediate product was not measured, but was hypothesized to be dissolved cellulose. The reaction scheme is

$$C + HF \xrightarrow{k_1} DC + HF \xrightarrow{k_2} G$$

where

C = solid cellulosic glucan

DC = dissolved cellulosic glucan

G = water-soluble glucan

A pseudo-first order reaction model was used for each of these reactions, yielding

$$C_C = C_{C_o} e^{-k_1 t}$$

$$C_{DC} = C_{C_o} \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

and

$$C_G = C_{C_o} - C_C - C_{DC}$$

A major complication experienced in obtaining the experimental data was that a constant temperature in the reaction vessel could not be maintained. This was due to the exothermic nature of the reaction coupled with the very low thermal conductivity of the thick-walled Kel-F reaction vessel, therefore requiring a more complicated analysis than would be needed for a truly isothermal reaction.

VII. RESULTS AND INTERPRETATION

A. GLUCOSE

As mentioned earlier, preliminary analysis of the results of HF saccharification of wood and cellulose at $0^{o}C$ (Selke et al, 1982) showed that the simple pseudo-first order rate model fit the data reasonably well as long as an initial delay time was added. These data also showed that the rate was not influenced by particle size between 60 mesh ground wood and the small chips, but that there was a considerable slowing of the rate between small and "large" (standard size) wood chips, presumably due to mass transfer effects. This earlier data will be resummarized below, with the addition of the new data and the more sophisticated analysis methods and model.

The simplest data analysis method used was linear regression on the pseudo-first order rate model with initial delay discussed earlier. The major difficulty with this approach is that the reaction temperature could not be maintained at a constant value, as mentioned earlier. Thus it was necessary to use a time-average temperature. The calculated rates for glucose, average temperatures, and "initial delay" are presented in Table 3, along with the

TABLE 3

REACTION RATES FOR GLUCOSE - MODEL 1

Substrate and conditions	Ave. Temp. (^{o}C)	Rate (min^{-1})	Initial Delay (min)	Corr. Coeff.
Filter paper, anhydrous	1.3	.235	.6	.896
	-1.9	.225	3.2	.978
	-9.5	.029	9.8	.991
	-11.9	.011	16.1	.924
Filter paper, 3.6% water	1.4	.109	2.7	.994
	0.3	.102	2.9	.973
	-7.4	.042	14.9	.983
	-9.0	.023	13.0	.952
Filter paper, 6.4% water	1.3	.066	3.0	.925
	-6.0	.013	2.8	.948
	-7.2	.025	5.3	.945
Wood, anhydrous	3.9	.179	1.4	.865
	-3.6	.079	5.0	.970
	-8.2	.063	12.6	.933
	-8.5	.061	11.2	.903
Wood, 3.6% water	3.1	.091	2.2	.921
	-9.1	.024	5.4	.951
	-9.6	.032	8.5	.953
	-10.6	.036	9.5	.969

TABLE 3 (cont'd.)

Wood, 6.4% water	2.5	.086	1.8	.959
	-6.2	.012	4.3	.692
	-6.4	.015	2.9	.950

correlation coefficient obtained. Figures 5-10 show the fit of the data to the calculated parameters. In this and in subsequent analyses, it was necessary to have the initial concentration of glucan in the substrate. Calculation for filter paper gave a value for C_{C_o} of 6.1675×10^{-3} moles glucan residues per g filter paper, based on the filter paper being 100% glucan residues. For wood the situation is more complex, since as discussed in Section V all available analysis methods for lignocellulose are at least somewhat unreliable. A value of 3.441×10^{-3} moles glucan residues per g wood was calculated based on average composition for our tree species, and was found to be in general agreement with our yield data for HF saccharification, so this was the value used for wood. In the figures, yields are normalized by dividing by the initial glucan concentration of the substrate. Sugar yield data and actual temperatures are presented in Appendix B. Activation energies and the preexponential factor calculated from these values are presented in Table 4. In general all data points after the initial delay time were used in the calculations, but on occasion points which significantly reduced the correlation coefficient and were obviously out of line with the other data were omitted.

The general trend seen is that the rate constant is higher for pure cellulose (filter paper) than for cellulose

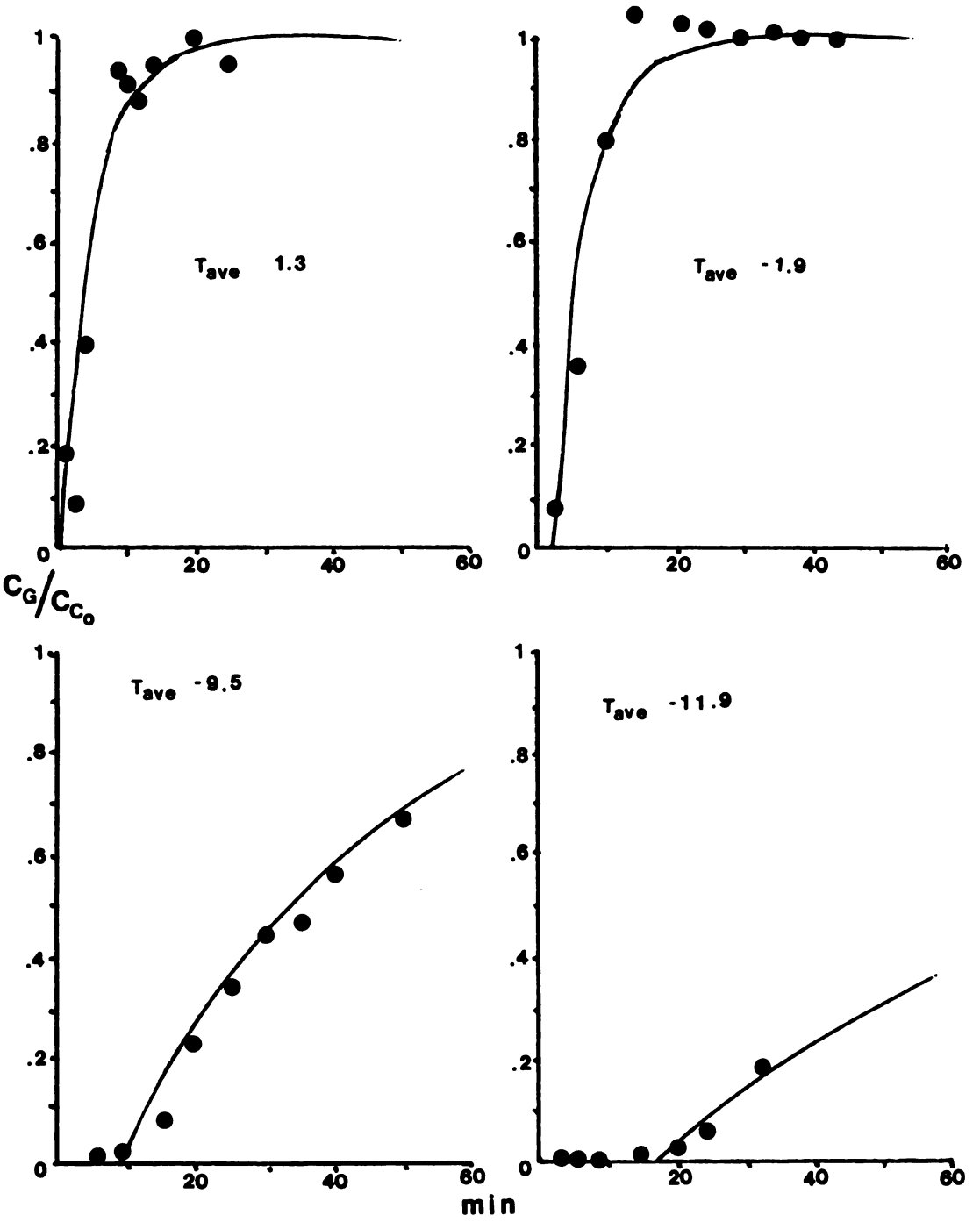


FIGURE 5

FILTER PAPER, ANHYDROUS HF - MODEL 1
(Conc. soluble glucan/initial conc. vs. time)

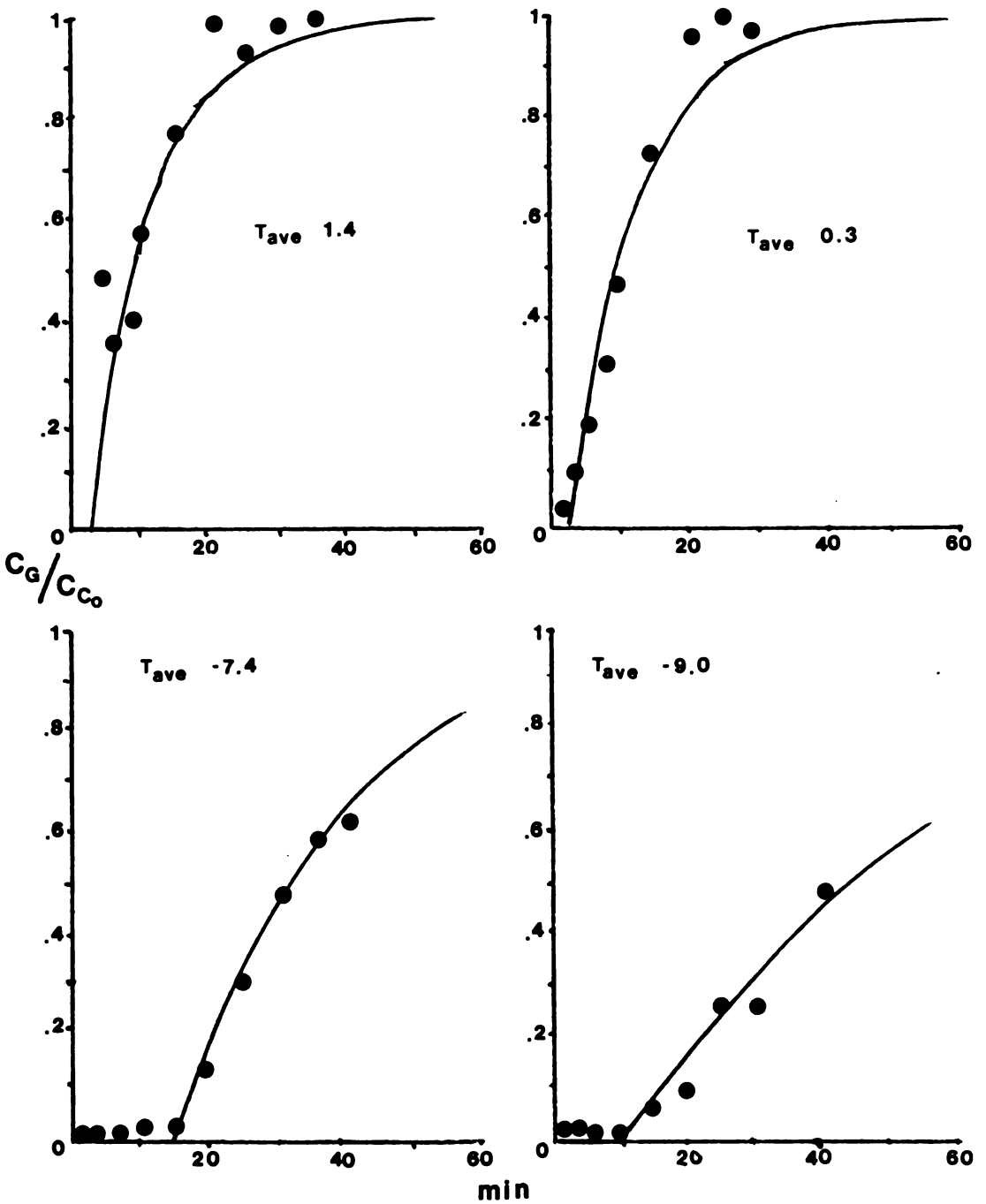


FIGURE 6

FILTER PAPER, HF WITH 3.6% WATER - MODEL 1
(Conc. soluble glucan/initial conc. vs. time)

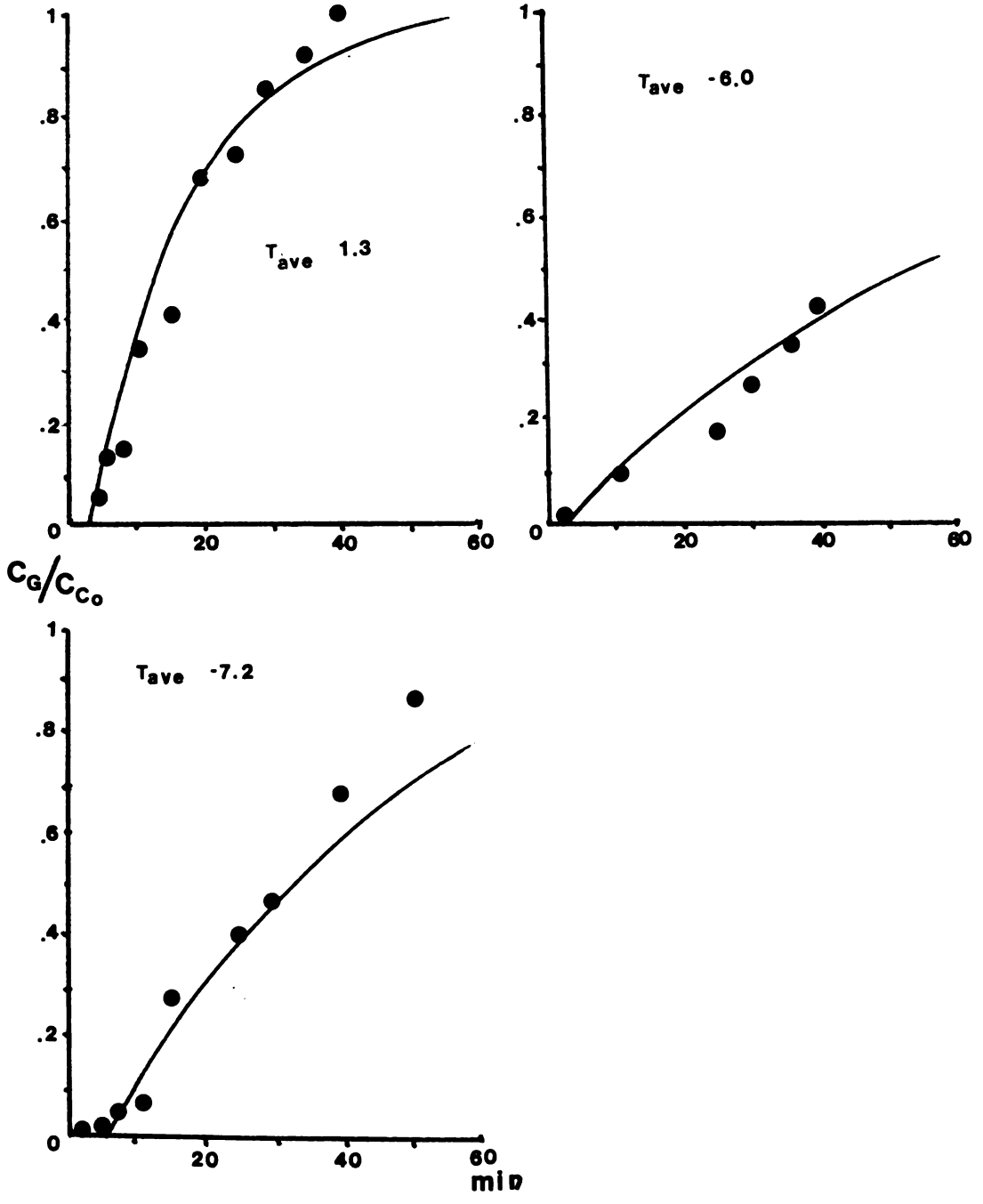


FIGURE 7

FILTER PAPER, HF WITH 6.4% WATER - MODEL 1
(Conc. soluble glucan/initial conc. vs. time)

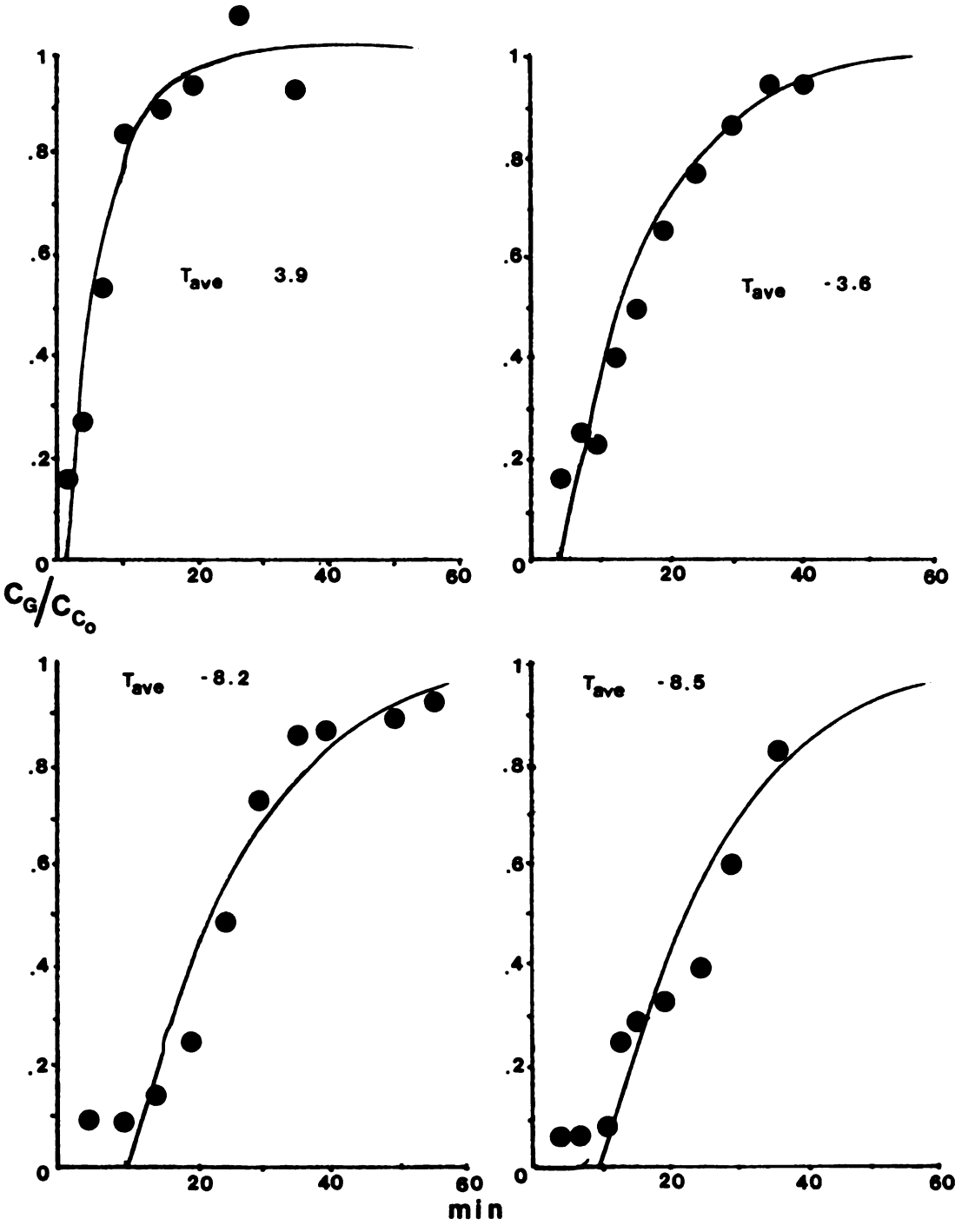


FIGURE 8

WOOD, ANHYDROUS HF - MODEL 1
(Conc. soluble glucan/initial conc. vs. time)

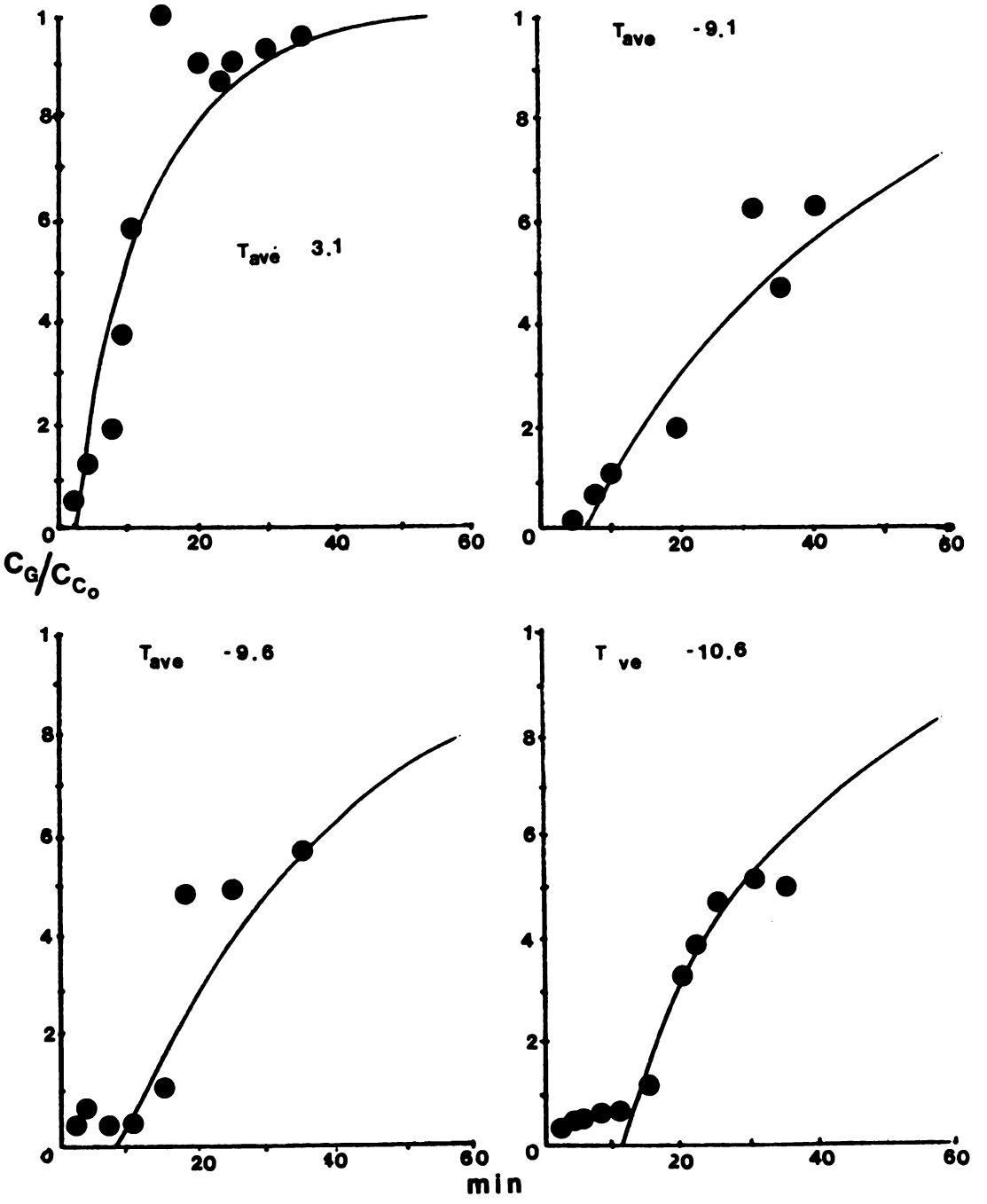


FIGURE 9

WOOD, HF WITH 3.6% WATER - MODEL 1
(Conc. soluble glucan/initial conc. vs. time)

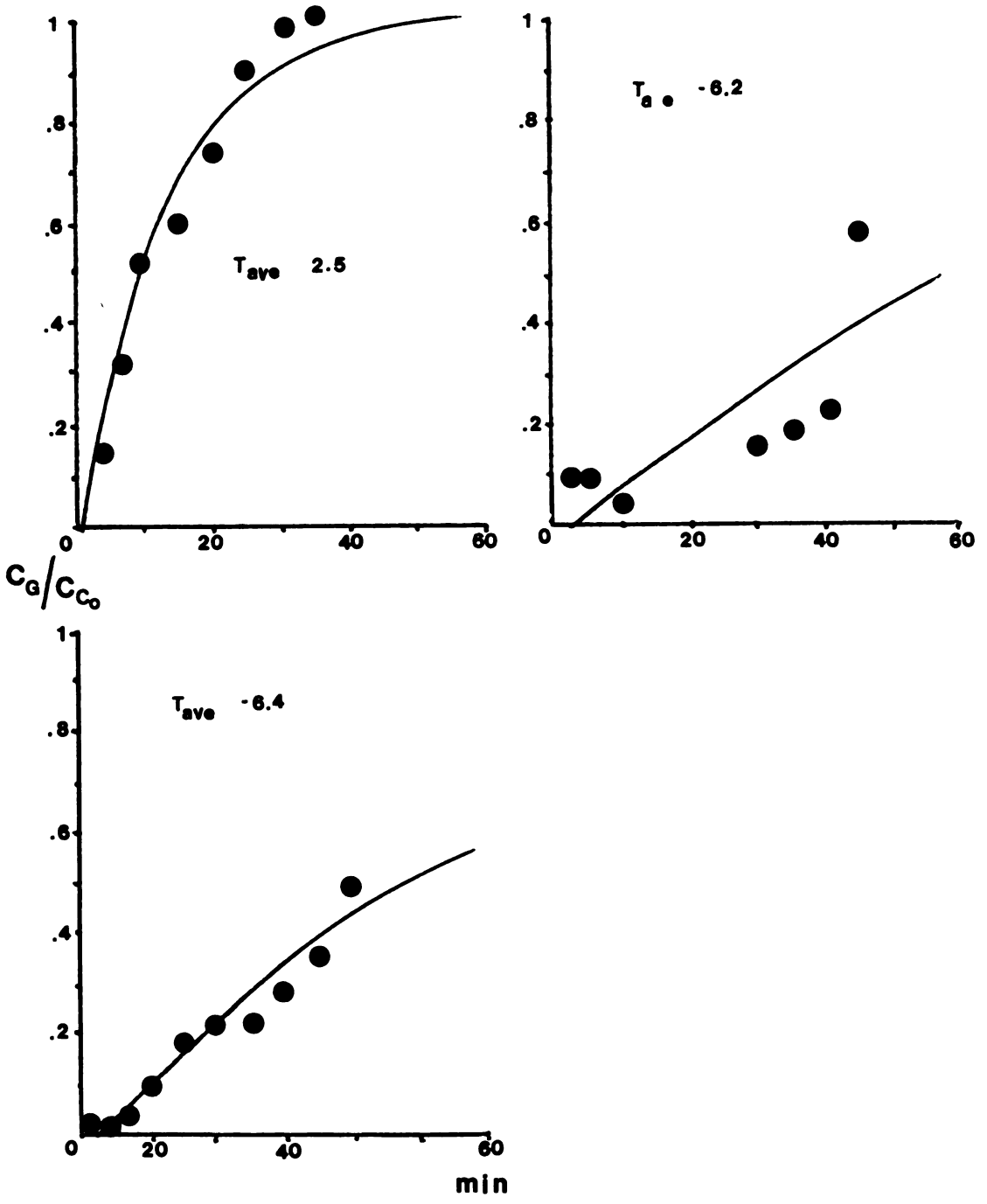


FIGURE 10

WOOD, HF WITH 6.4% WATER - MODEL 1
(Conc. soluble glucan/initial conc. vs. time)

TABLE 4

ACTIVATION ENERGIES FOR GLUCOSE - MODEL 1

$$k = Ae^{-E_a/RT}$$

Substrate and conditions	ln A	E_a (kcal)	Corr. Coeff.
Filter paper, anhydrous	61.54	34.20	.977
Filter paper, 3.6% water	34.39	19.97	.978
Filter paper, 6.4% water	37.67	22.10	.855
Wood, anhydrous	20.87	12.49	.984
Wood, 3.6% water	19.26	11.92	.923
Wood, 6.4% water	53.75	30.84	.992
(without second data set	49.90	28.72)	

in wood, which is in agreement with the information on acid hydrolysis of wood. The initial delay parameter increases with decreasing temperature, while the rate decreases with decreasing temperature. This is also behavior to be expected if the "initial delay" represents a solubilization step, which would be slower at colder temperatures.

Another trend is for the rate to decrease with increasing water concentration. The activation energy appears to be about the same for 3.6% and 6.4% water with filter paper, and about 10 kcal higher for anhydrous HF with filter paper. For wood, the activation energy is nearly the same for the anhydrous and 3.6% water cases, with 6.4% water giving an anomalously high activation energy which predicts a rate constant at 10^{o}C actually higher than that for anhydrous HF (see Table 6).

One of the major problems with the preceding analysis is that the temperature in the reaction mixture is <u>not</u> constant at the average temperature listed. This can introduce sizable inaccuracies into the data analysis, since the temperature commonly varied by 2-3 degrees and in some cases by considerable more (see Appendix 2).

Therefore the next method of data analysis was chosen to allow the incorporation of the temperature dependence of the rate (in an Arrhenius form). The KINFIT4 program developed at Michigan State University by Dr. James Dye

and others (Dye and Nicely, 1971) is a nonlinear curve-fitting program which allowed incorporation of these temperature fluctuations. In this method, the temperature between each two sample times was regarded as constant at its average value, thereby considerably limiting the temperature variation for each rate calculation - usually to less than half a degree and often to a tenth of a degree or less. Values were obtained for the rate constants at $10^{o}C$ and for the activation energies, and are presented in Table 5. Figures 11-16 show the fit of the data to the caclulated parameters. The initial delay was allowed to vary for each run.

As can be seen, the general trend is for the initial delay to increase with decrease in temperature and with increase in water concentration. The rate constants themselves at $10^{o}C$ show a slight tendency to increase with increasing water concentration, a consequence of the increase in activation energy with water concentration which is calculated to occur, and therefore quite possibly a figment of extrapolation beyond the range of the data. The rate constants from the two models calculated at $10^{o}C$, $0^{o}C$ and $-5^{o}C$ are presented in Table 6. As can be seen, both the rate constants and the activation energies from the two models are fairly close in most instances, indicating that the use of an overall time-average temperature

TABLE 5

REACTION RATES FOR GLUCOSE - MODEL 2*

Substrate and conditions	k (min^{-1})	E_a (kcal)	Initial Delay
Filter paper, anhydrous	.447 (.094)	17.8 (2.4)	
1.3°C			0.
-1.9°C			0.
-9.5°C			24.3 (3.0)
-11.9°C			13.5 (1.9)
Filter paper, 3.6% water	.553 (.170)	23.5 (3.6)	
1.4°C			3.9 (.7)
0.3°C			3.9 (.5)
-7.4°C			14.0 (2.7)
-9.0°C			17.4 (1.9)
Filter paper, 6.4% water	.130 (.029)	12.6 (2.7)	
1.3°C			3.8 (.6)
-6.0°C			22.1 (1.9)
-7.2°C			6.6 (1.6)
Wood, anhydrous	.278 (.076)	14.2 (2.7)	
3.9°C			1.0 (.6)
-3.6°C			6.0 (.8)
-8.2°C			12.2 (1.8)
-8.5°C			9.7 (1.1)

TABLE 5 (cont'd.)

Wood, 3.6% water	.289 (.097)	15.8 (2.9)	
3.1°C			3.6 (.8)
-9.1°C			5.3 (2.)
-9.6°C			6.1 (2.)
-10.6°C			8.9 (2.7)
Wood, 6.4% water	.376 (.128)	28.1 (4.2)	
2.5°C			1.4 (1.1)
-6.2°C			20.7 (3.9)
-6.4°C			6.9 (2.0)

* Numbers in parentheses are marginal standard deviations

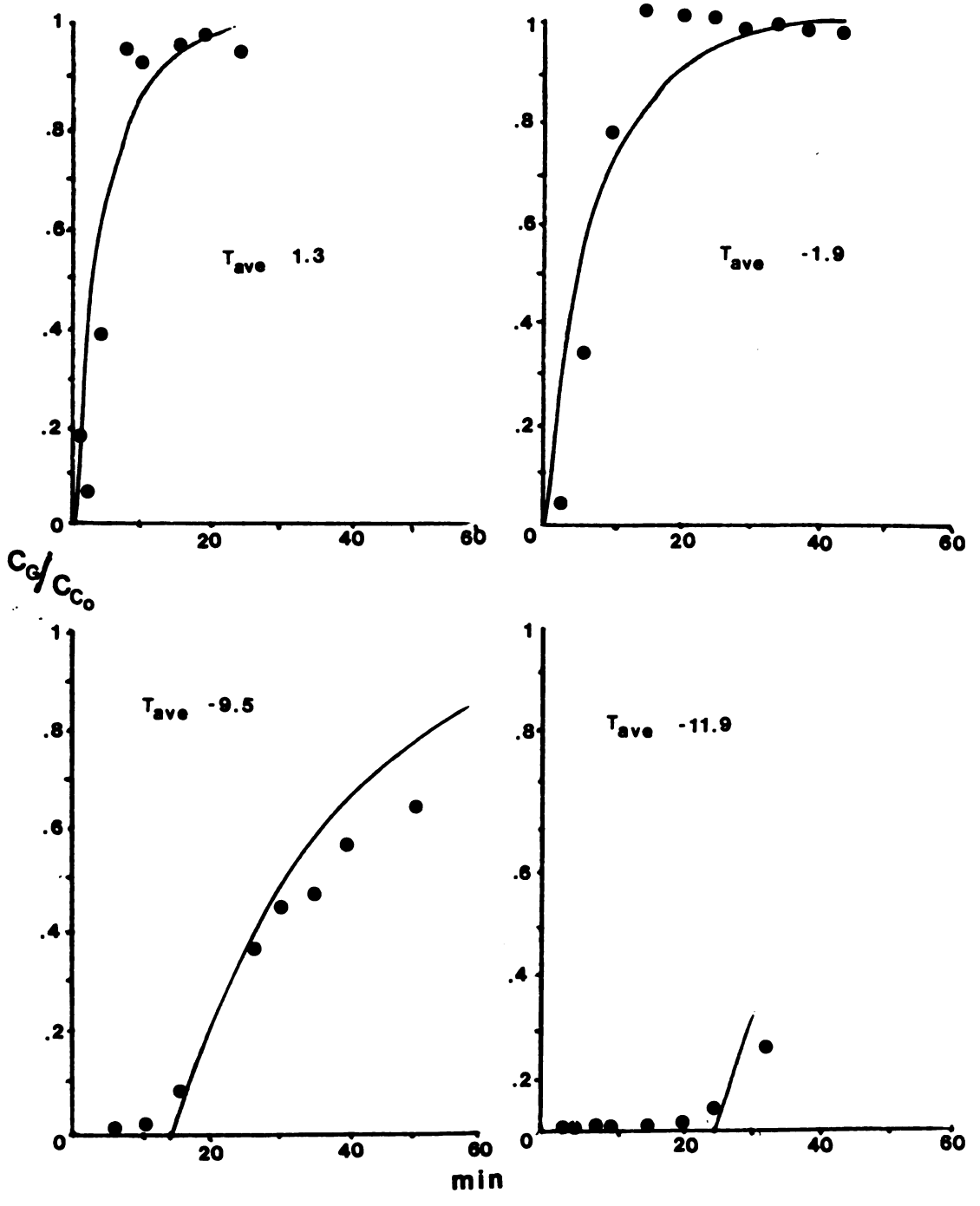


FIGURE 11

FILTER PAPER, ANHYDROUS HF - MODEL 2
(Conc. soluble glucan/initial conc. vs. time)

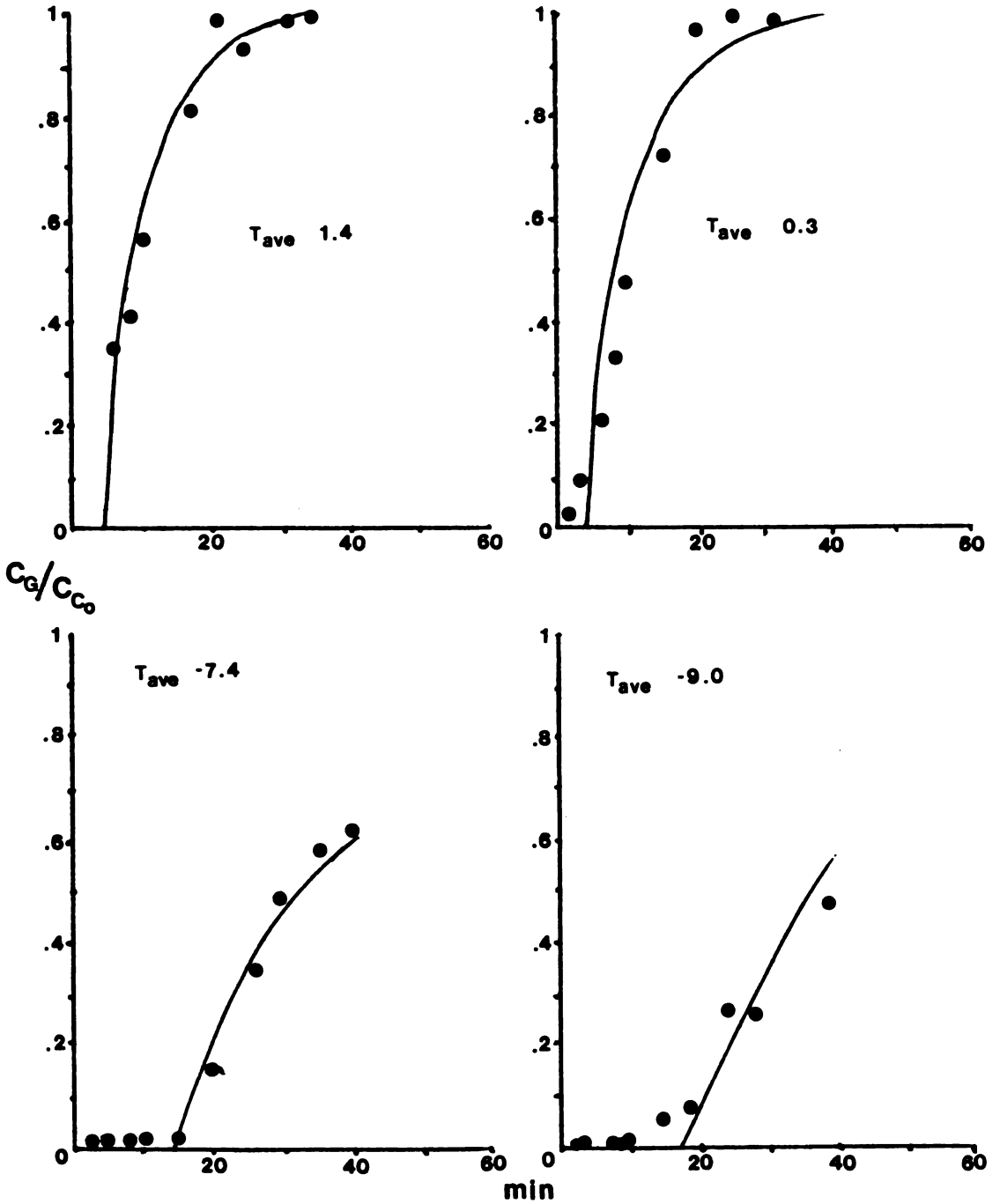


FIGURE 12

FILTER PAPER, HF WITH 3.6% WATER - MODEL 2
(Conc. soluble glucan/initial conc. vs. time)

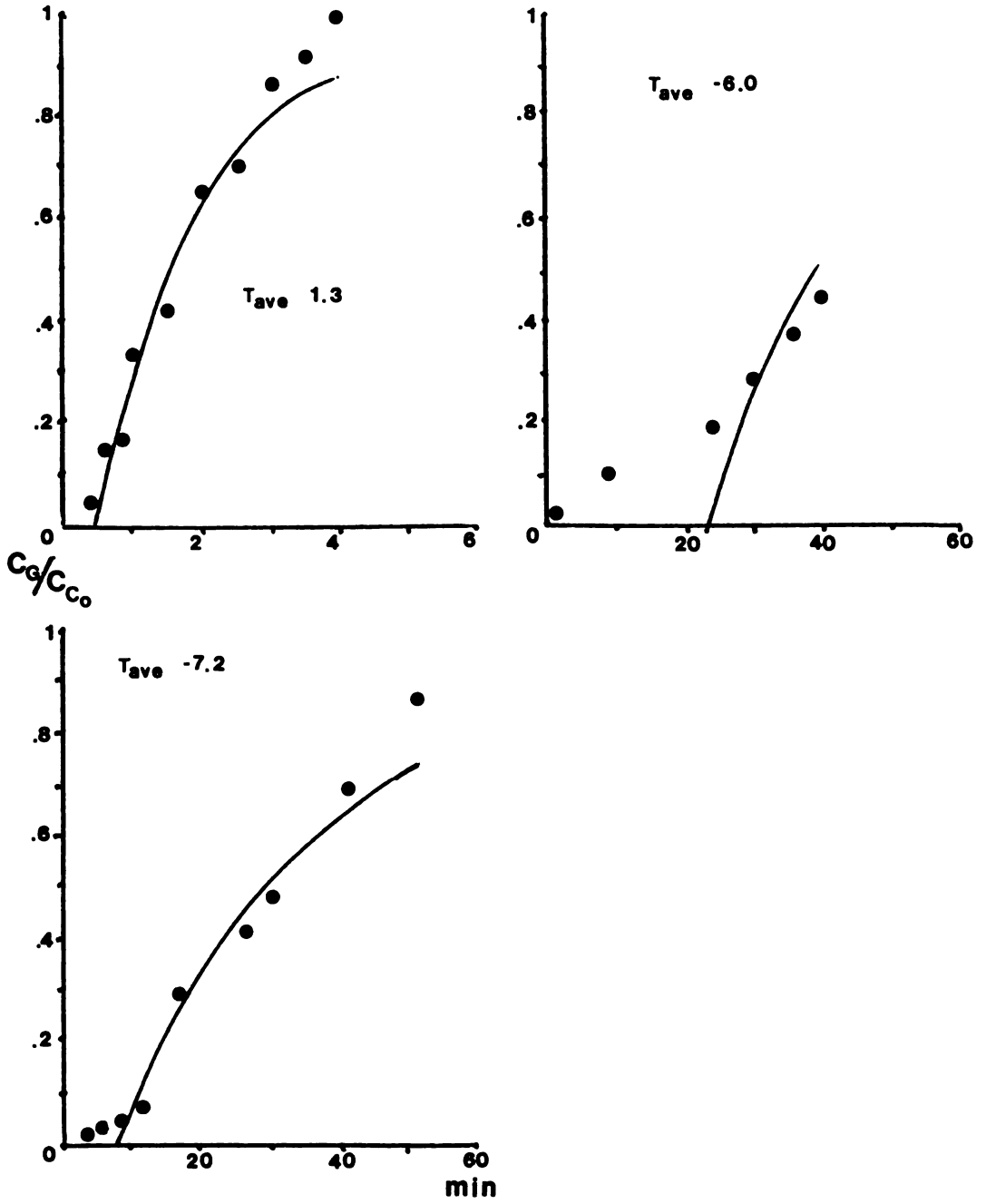


FIGURE 13

FILTER PAPER, HF WITH 6.4% WATER - MODEL 2
(Conc. soluble glucan/initial conc. vs. time)

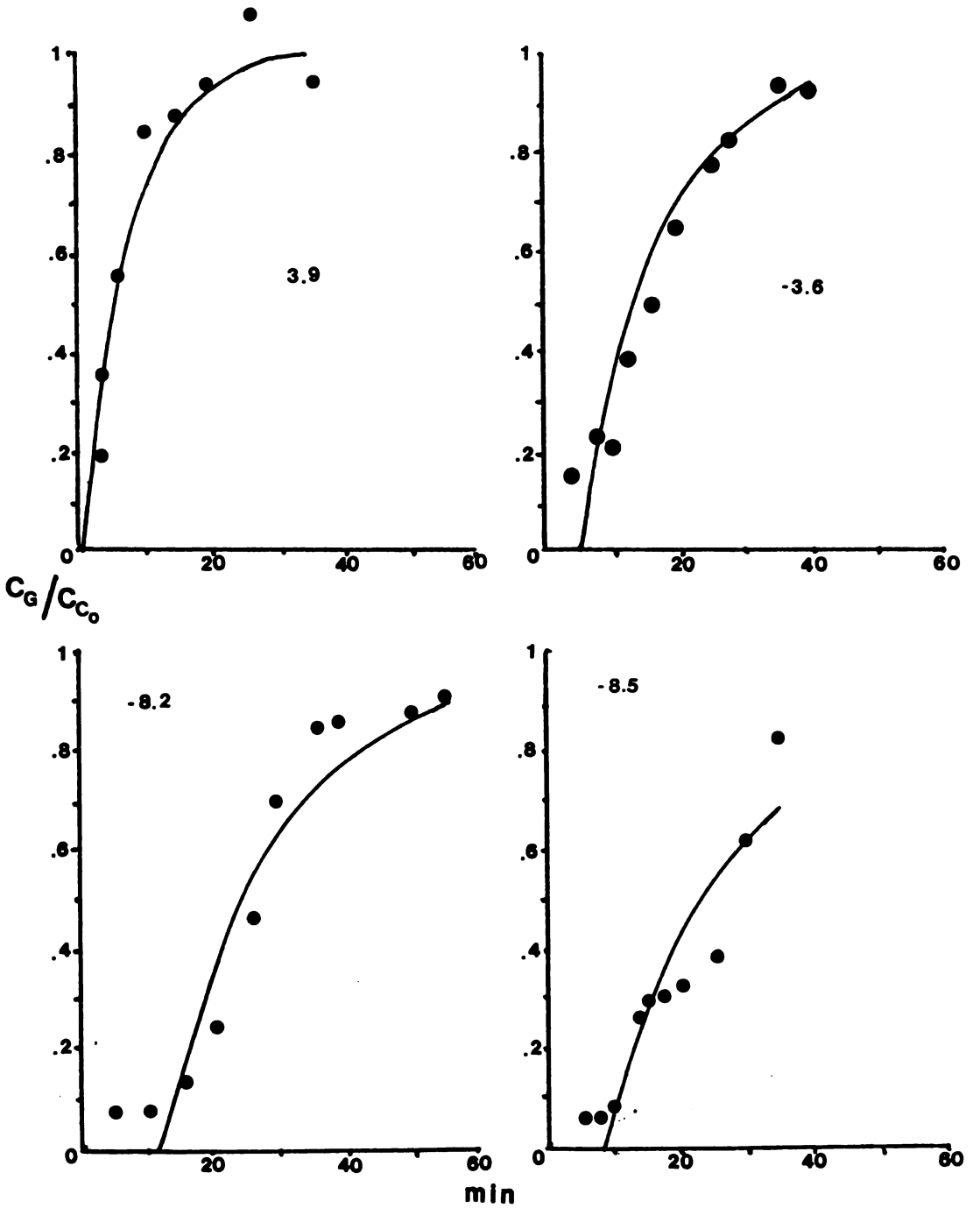


FIGURE 14

WOOD, ANHYDROUS HF - MODEL 2
(Conc. soluble glucan/initial conc. vs. time)

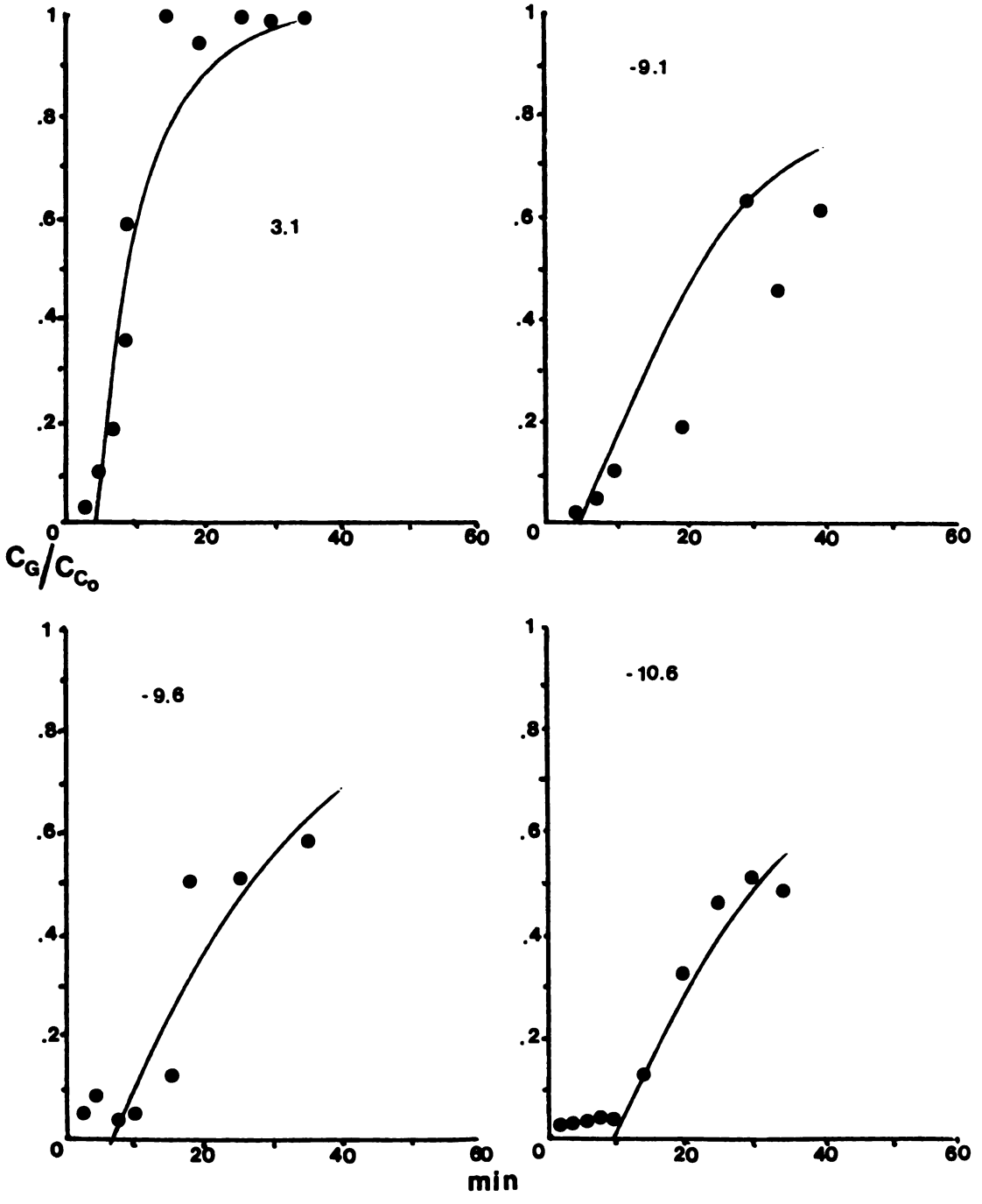


FIGURE 15

WOOD, HF WITH 3.6% WATER - MODEL 2
(Conc. soluble glucan/initial conc. vs. time)

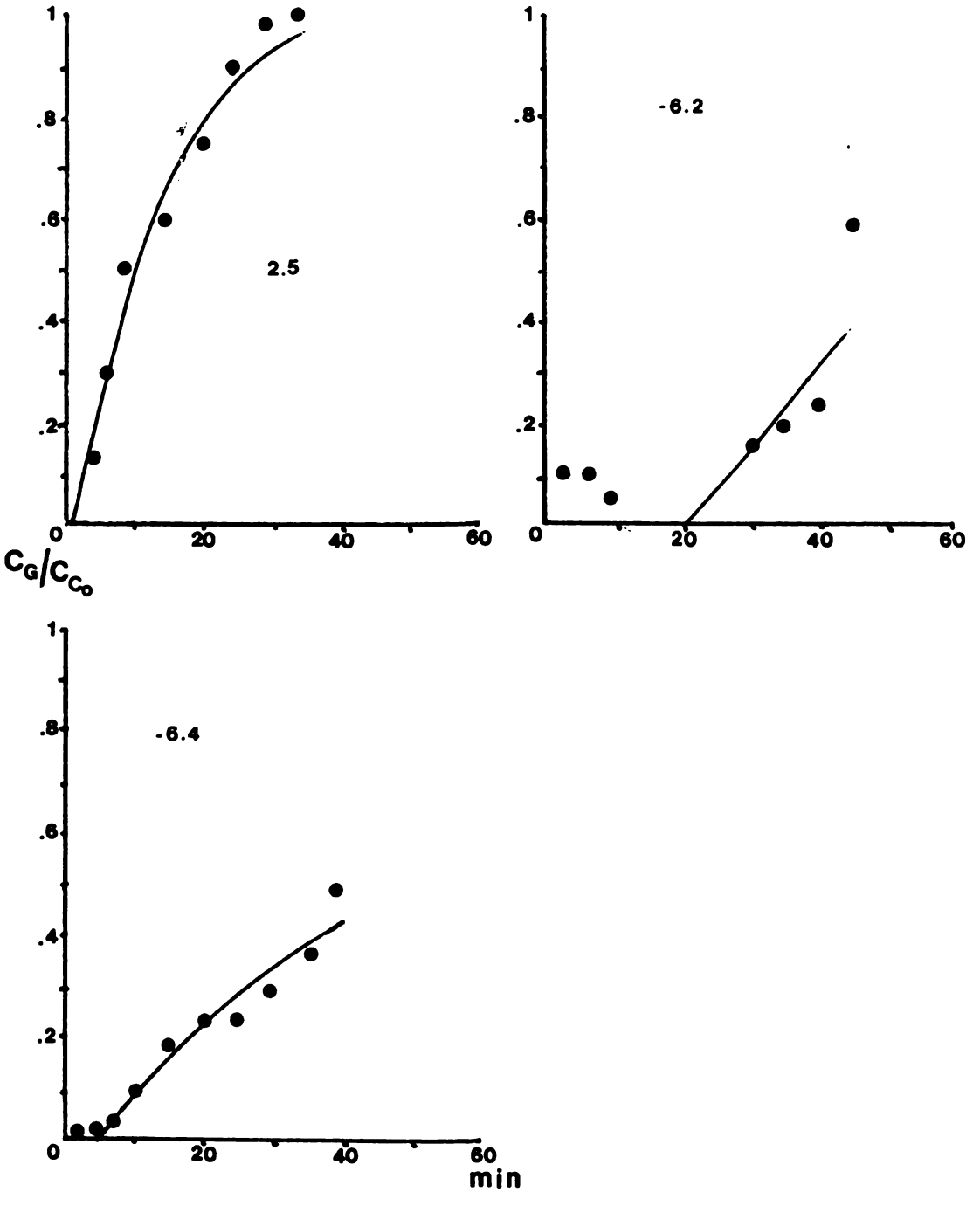


FIGURE 16

WOOD, HF WITH 6.4% WATER - MODEL 2
(Conc. soluble glucan/initial conc. vs. time)

TABLE 6

COMPARISON OF GLUCOSE RATES

Substrate and Model	Temperature 10°C	0°C	-5°C
Filter paper, anhydrous			
Model 1	2.21	.240	.074
Model 2	.45	.141	.076
Filter paper, 3.6% water			
Model 1	.35	.095	.048
Model 2	.55	.120	.054
Filter paper, 6.4% water			
Model 1	.21	.051	.024
Model 2	.13	.057	.037
Wood, anhydrous			
Model 1	.28	.123	.080
Model 2	.28	.111	.068
Wood, 3.6% water			
Model 1	.15	.069	.046
Model 2	.29	.104	.060
Wood, 6.4% water			
Model 1	.34	.051	.018
Model 2	.38	.061	.023

in Model 1 was fairly successful.

The next step in the data analysis was a reevaluation of the initial delay parameter. If, as hypothesized, this represented a requirement for the cellulose to dissolve before reaction, then the dissolving process, which involves breaking the intermolecular hydrogen bonds and disruption of the crystalline structure of the cellulose, could be treated as a reaction with its own rate constant and activation energy. Therefore this sequential reaction model was tested, again using the KINFIT4 program. The rate constant and activation energy for the dissolving of the cellulose were termed k_1 and E_{a1} and those for the reaction with HF termed k_2 and E_{a2}. Calculated values are presented in Table 7, with Figures 17-22 showing the data fit.

As can be seen, one of the major problems with this analysis is the very large size of the marginal standard deviations (i.e. the standards deviations allowing all other parameters to vary as well). This results primarily from the very high degree of correlation of the parameters with each other (as high as .99999 in some cases). Unfortunately, with only one measurable product, there is no apparent way to uncouple these parameters.

A variation of this analysis was to consider that dissolved cellulose from wood and dissolved cellulose from

TABLE 7

GLUCOSE RATES - SEQUENTIAL MODEL

Substrate	k_1	σ	E_{a1}	σ	k_2	σ	E_{a2}	σ
Filter pap., anhydr.	6.67	6.7	40.6	7.9	.54	.28	15.2	7.6
Wood, anhydr.	.36	.34	13.7	12.2	.77	1.09	20.2	12.6
F. Pap., 3.6%	.65	10.8	22.1	13.8	.69	11.9	23.2	17.3
Wood, 3.6%	.56	1.15	21.2	15.7	.18	.33	0.6	15.7
*F. Pap., 6.4%	1.13	1.23	31.6	11.1	.07	.06	-2.0	15.9
Wood, 6.4%	12.2	15.8	53.0	13.5	.27	.15	21.5	11.4
*without 2nd data set	.63	1.94	32.0	25.6	.15	.60	3.6	37.6

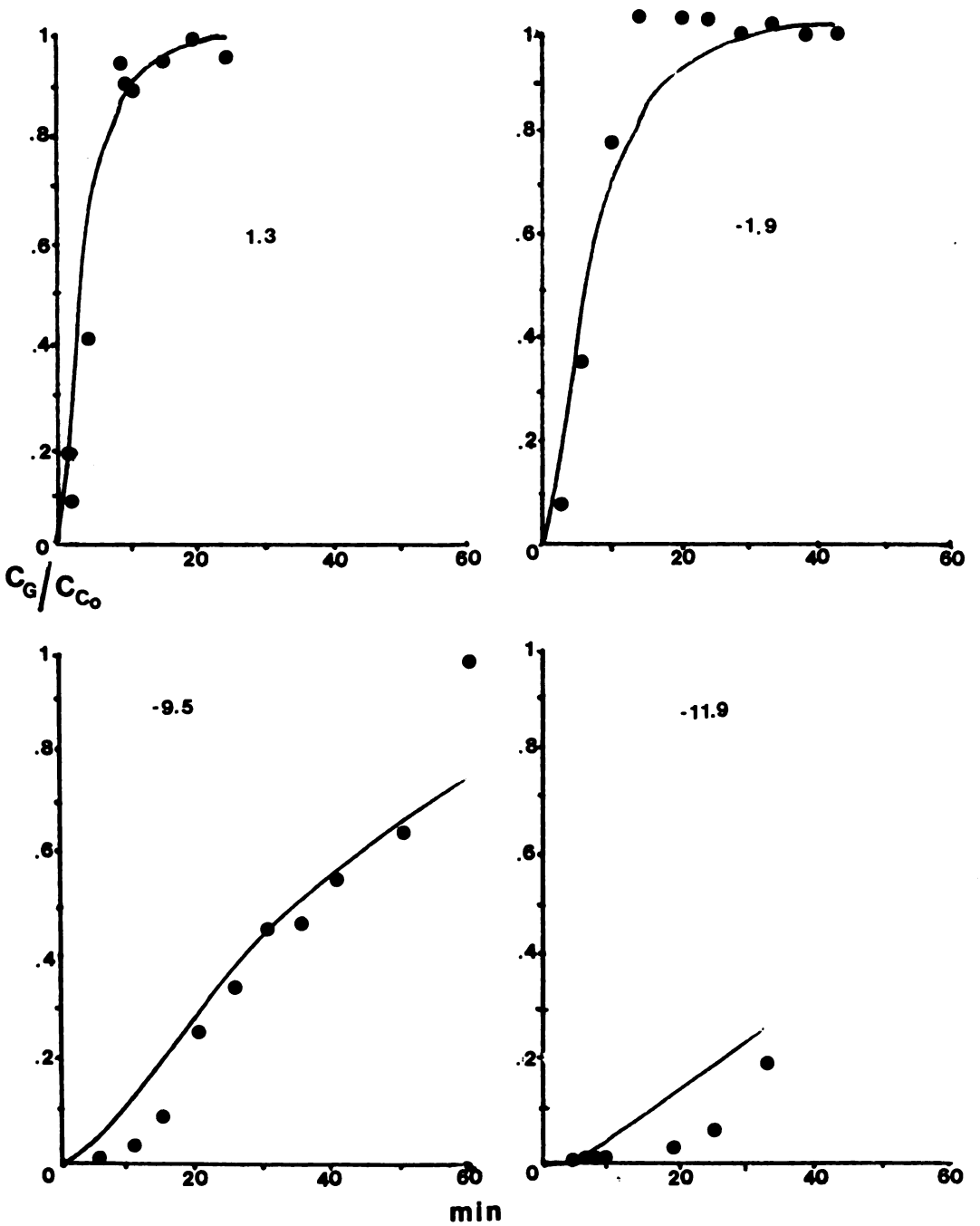


FIGURE 17

FILTER PAPER, ANHYDROUS HF - SEQUENTIAL MODEL
(Conc. soluble glucan/initial conc. vs. time)

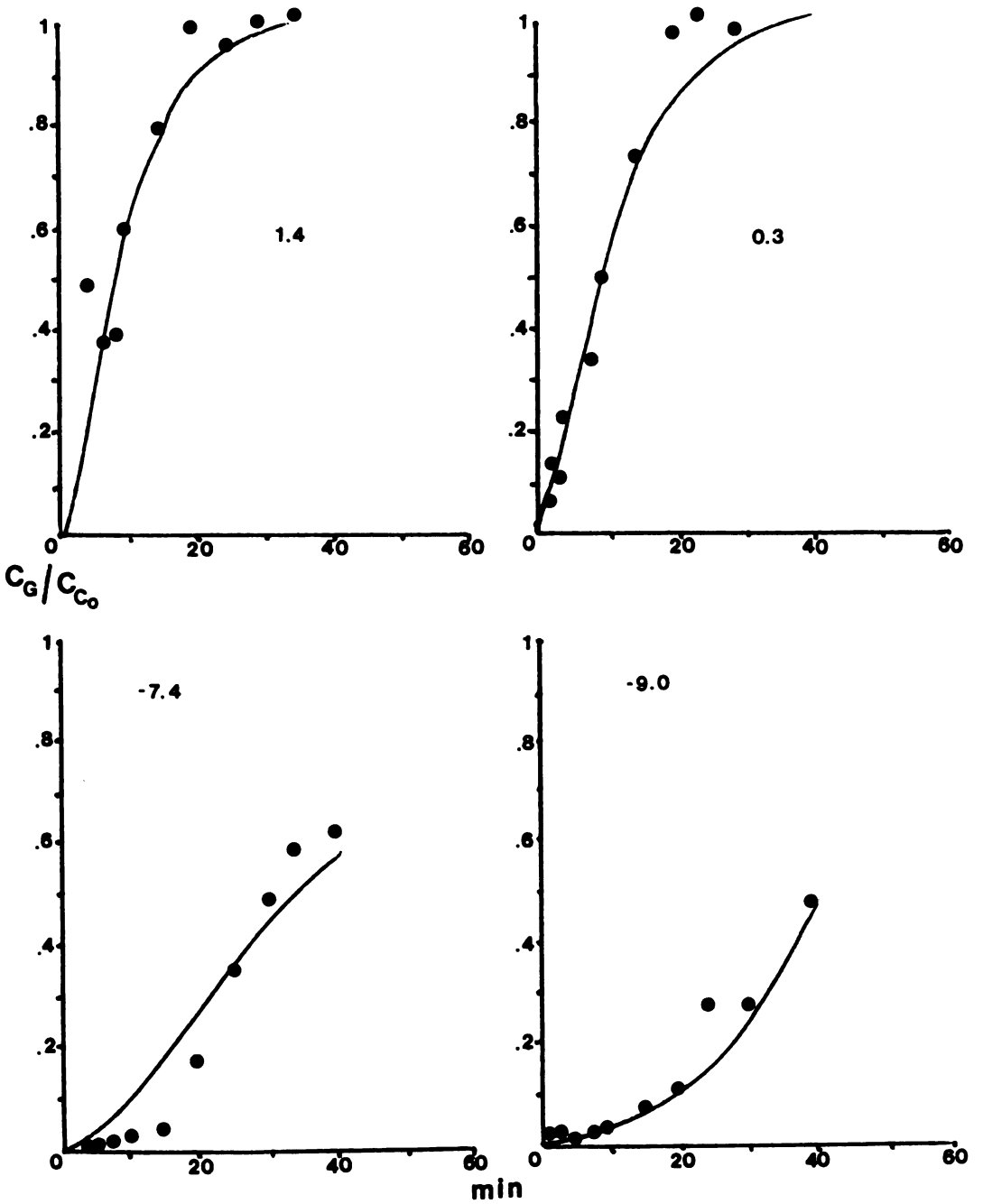


FIGURE 18

FILTER PAPER, HF WITH 3.6% WATER - SEQUENTIAL MODEL
(Conc. soluble glucan/initial conc. vs. time)

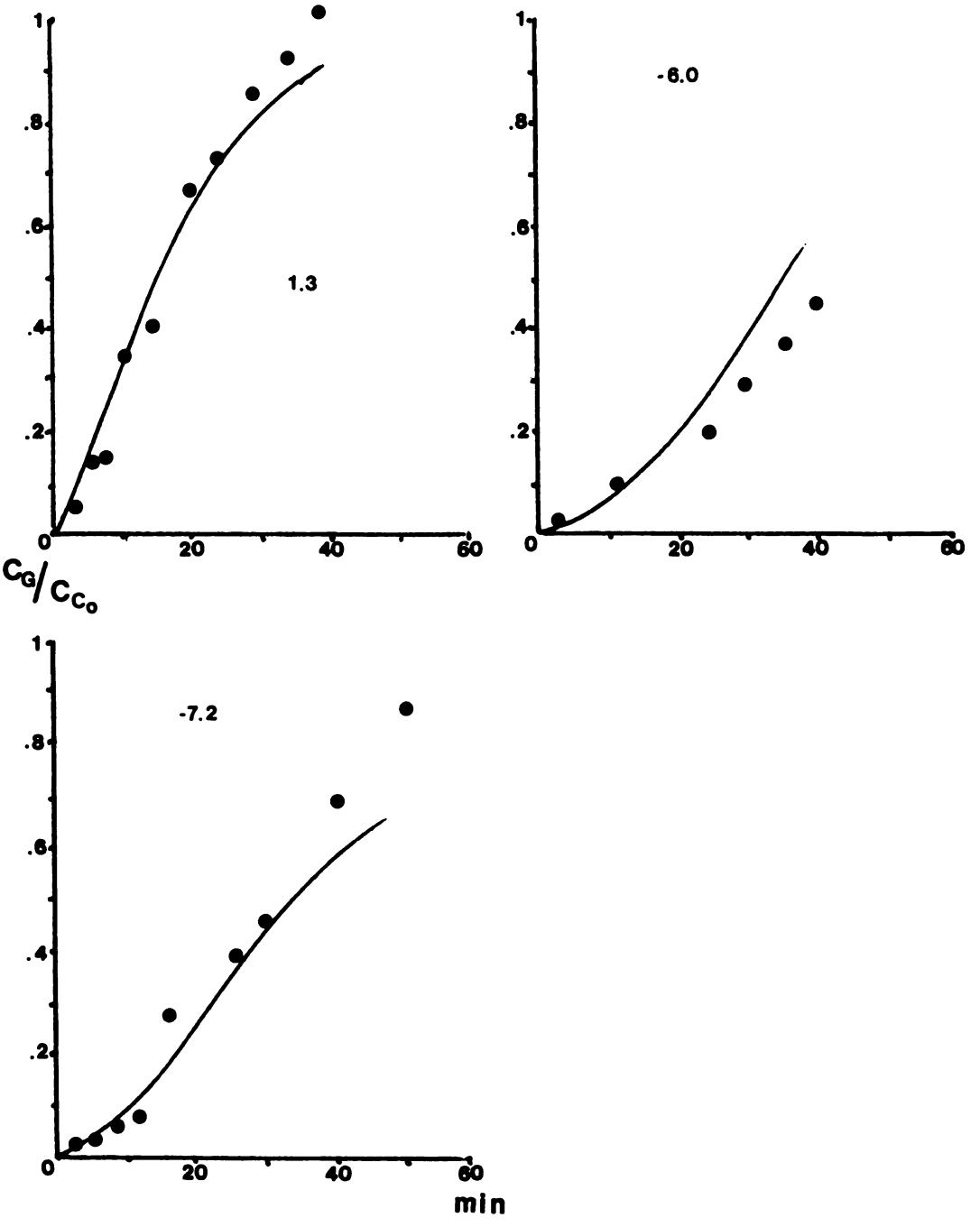


FIGURE 19

FILTER PAPER, HF WITH 6.4% WATER - SEQUENTIAL MODEL
(Conc. soluble glucan/initial conc. vs. time)

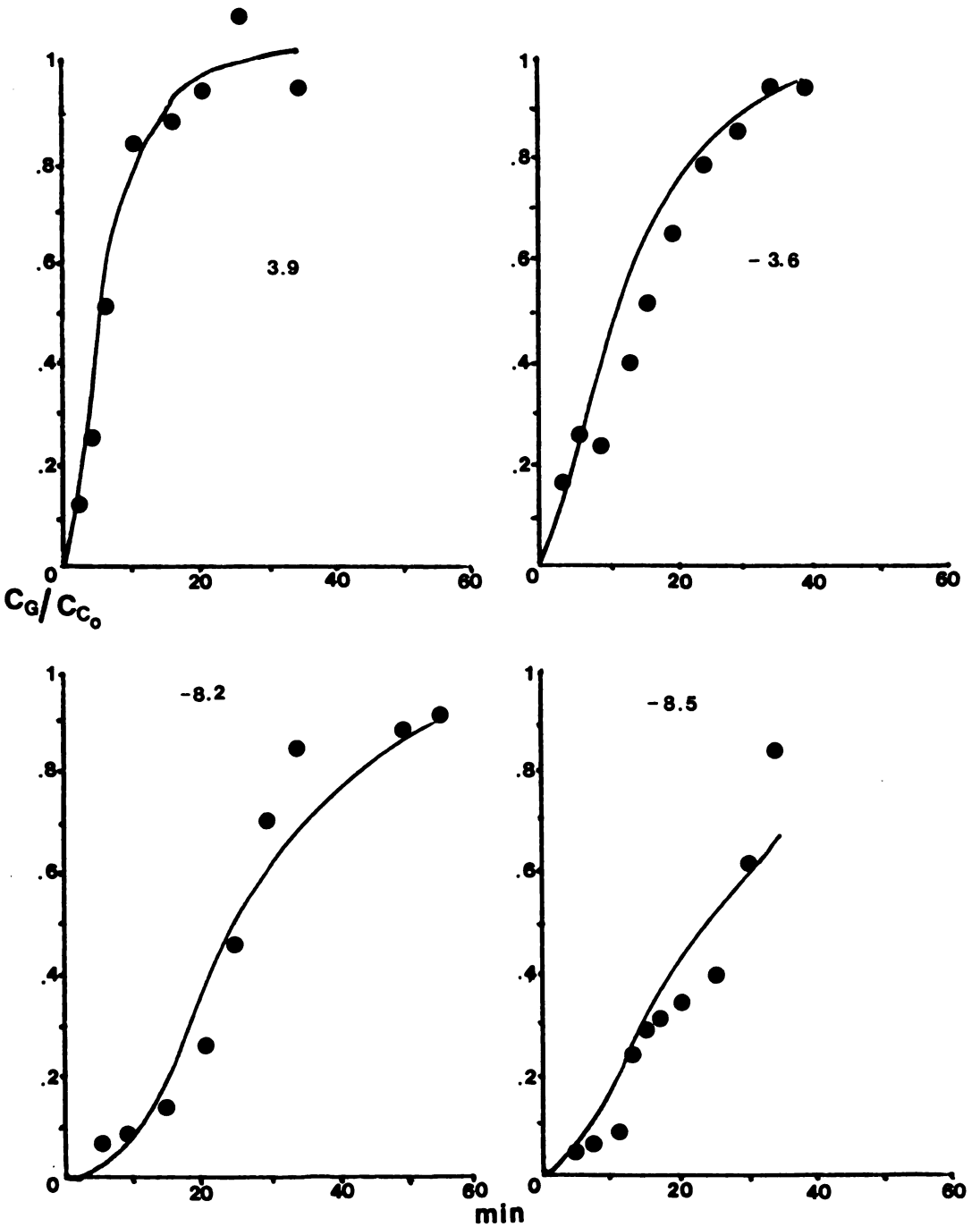


FIGURE 20

WOOD, ANHYDROUS HF - SEQUENTIAL MODEL
(Conc. soluble glucan/initial conc. vs. time)

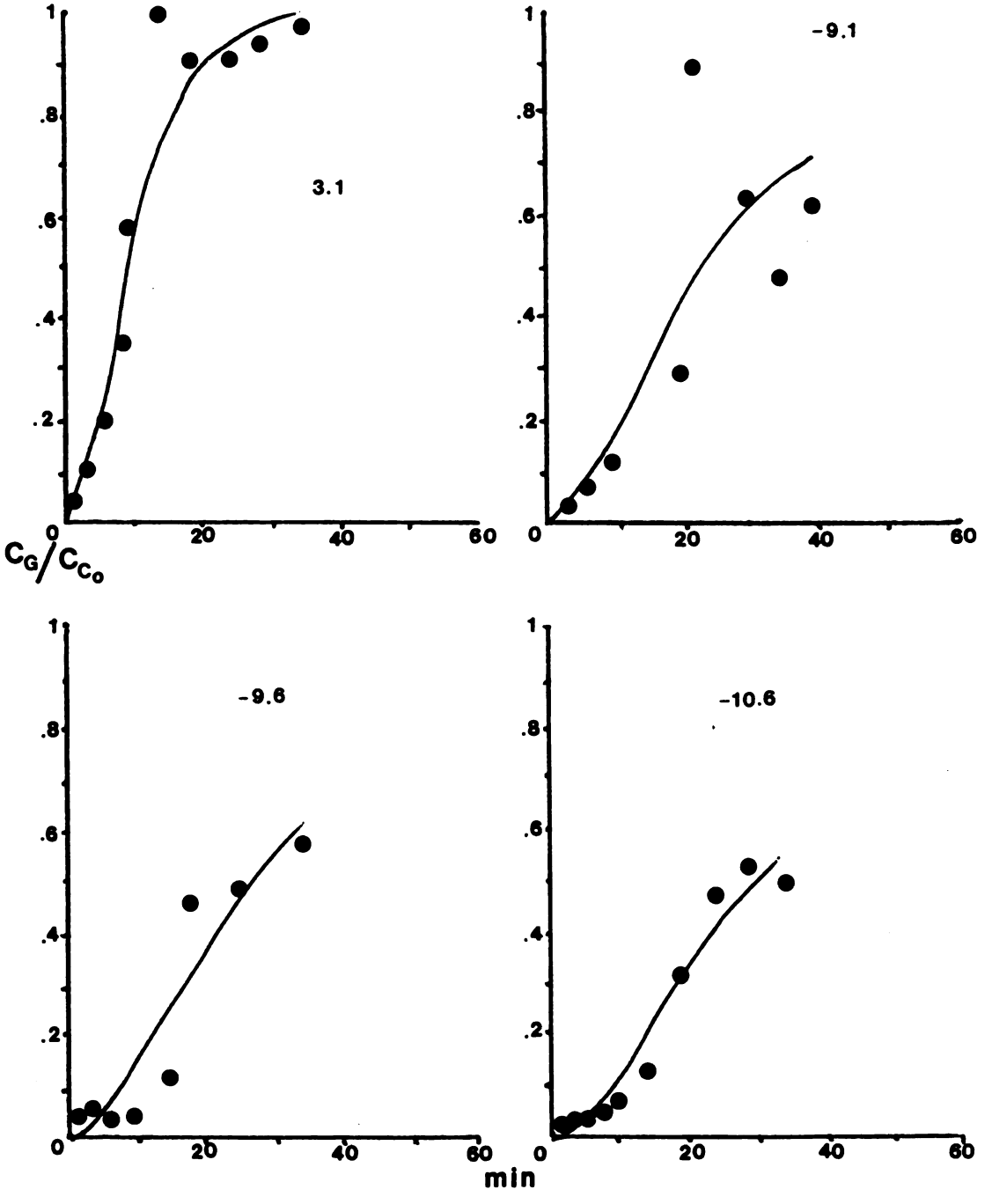


FIGURE 21

WOOD, HF WITH 3.6% WATER - SEQUENTIAL MODEL
(Conc. soluble glucan/initial conc. vs. time)

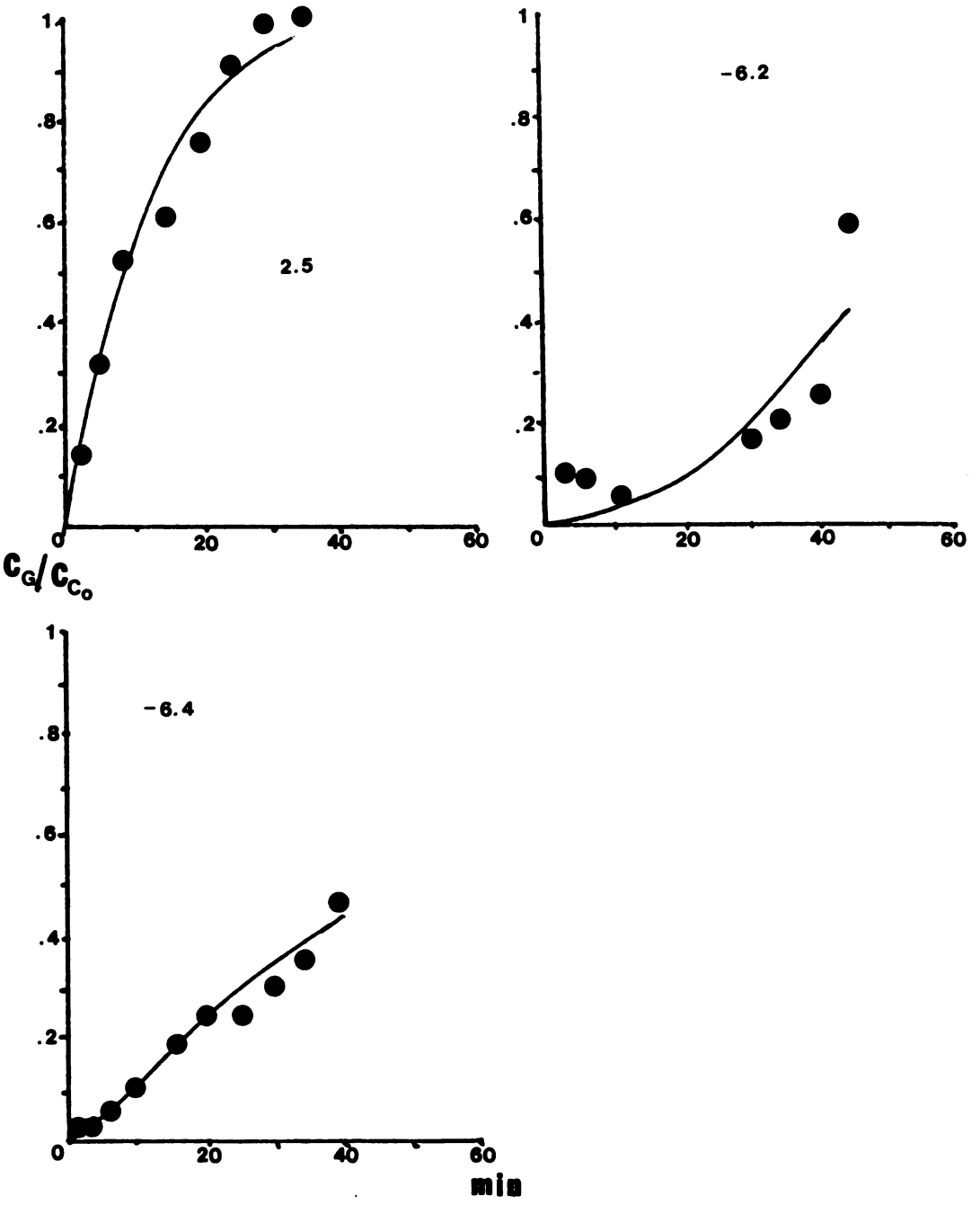


FIGURE 22

WOOD, HF WITH 6.4% WATER - SEQUENTIAL MODEL
(Conc. soluble glucan/initial conc. vs. time)

filter paper are likely to be chemically similar, so might be expected to react at the same rate. Therefore the sequential model modified to have k_2 and E_{a2} the same for both filter paper and wood was tested. In the anhydrous case, the results in Table 8 were obtained. The dissolution rate is much higher for filter paper than for wood, as was expected. Interestingly, the standard deviations of the parameters were decreased significantly, so this appeared to be a definite improvement on the individual sequential models. The predicted curves and actual values are shown in Figures 23 and 24. Unfortunately this model could not be extended to the 3.6% and 6.4% water cases, as it failed to converge.

Thus it appears that with the data presently available the two simplest models provide the best description. The "initial delay" parameter is artificial, but serves much the same function (though opposite in effect) as the instantaneous reaction of amorphous cellulose in the kinetic model for dilute acid hydrolysis. One fortunate factor is that as temperature increases the "delay time" decreases, and is likely to be near zero at the desired operating conditions for HF hydrolysis.

Another important factor to be evaluated is the dependence of the rate on water concentration. As has been mentioned, there is some tendency for the delay time to

TABLE 8

COMBINED MODEL

Substrate	k_1	σ	E_{a1}	σ
Filter paper, anhydrous	6.28	4.99	39.7	6.3
Wood, anhydr.	.43	.20	16.4	5.6
Wood + FP, anhydr.		k_2 =	.59	.24
		E_{a2}=	16.4	6.0

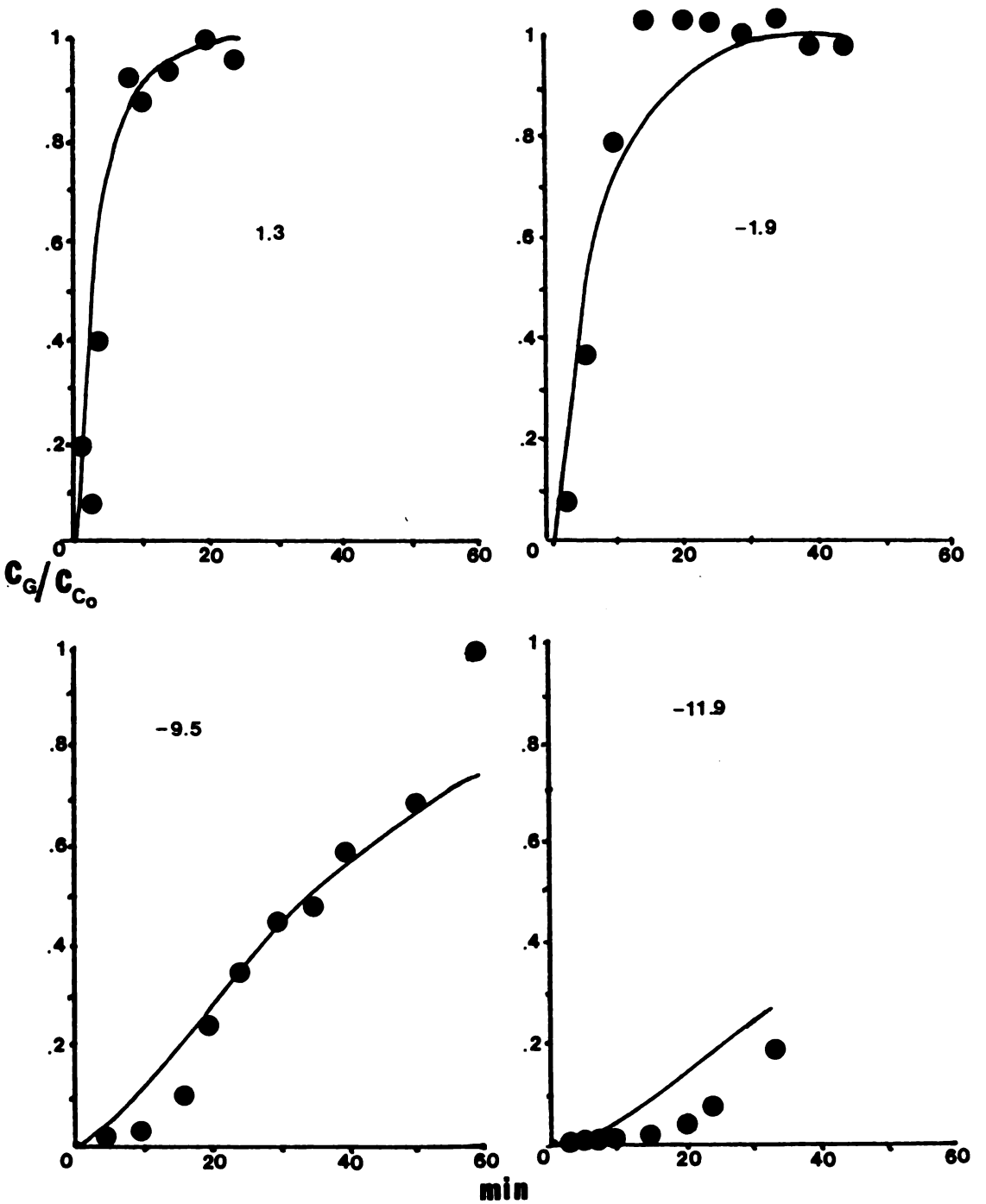


FIGURE 23

FILTER PAPER, ANHYDROUS HF - COMBINED MODEL
(Conc. soluble glucan/initial conc. vs. time)

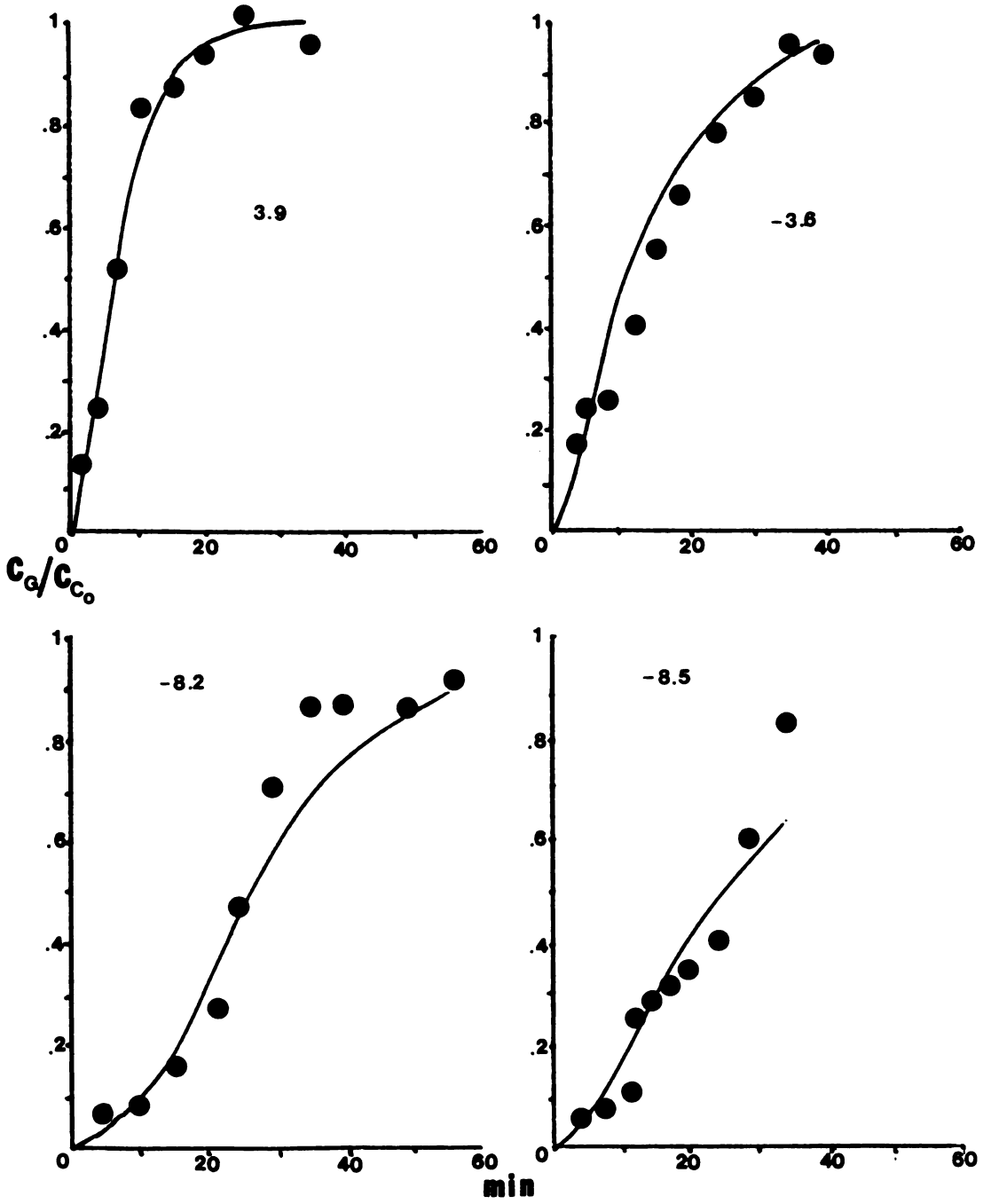


FIGURE 24

WOOD, ANHYDROUS HF - COMBINED MODEL
(Conc. soluble glucan/initial conc. vs. time)

increase with increasing water concentration and a definite tendency for the reaction rate to decrease.

To minimize the dangers of extrapolation and more accurately evaluate the effect of water concentration, the comparison will be made using the calculated rates in Table 6 for $0^{o}C$ and $-5^{o}C$, which are within the range of the data. It can be seen that the rate constant generally increases with decreasing water concentration. By analogy with acid hydrolysis of cellulose and of glycosyl fluorides, we would expect this dependence to be related to the Hammett acidity function, specifically a proportionality between log k and $-H_o$, the Hammett acidity (Bunton et al, 1955; Overend, 1972; Timell, 1964). By interpolation of data given by Hyman (Hyman et al, 1957) H_o for our three cases was calculated and is shown in Table 9, along with values of log k. These are graphed in Figures 25 and 26.

It is apparent that there is a significant deviation from a linear relationship with a slope of 1 as predicted from the cyclic oxocarbonium ion intermediate mechanism proposed by Defaye et al (1983). It this is confirmed, it will cast doubt on this mechanism.

A word of caution is needed here. This method of data analysis looked at all soluble sugars as reaction products. It is there fore possible that the true reaction rates at lower temperatures and at higher water

TABLE 9

HAMMETT ACIDITY AND LOG K

Substrate	H_o	Log k			
		0°C		-5°C	
		Model 1	Model 2	Model 1	Model 2
Filter paper					
Anhydr.	-10.	- .62	- .85	-1.13	-1.12
3.6%	-8.51	-1.02	- .92	-1.32	-1.27
6.4%	-8.38	-1.29	-1.24	-1.62	-1.43
Wood					
Anhydr.	-10.	- .91	- .96	-1.10	-1.17
3.6%	-8.51	-1.16	- .98	-1.34	-1.22
6.4%	-8.38	-1.29	-1.22	-1.75	-1.64

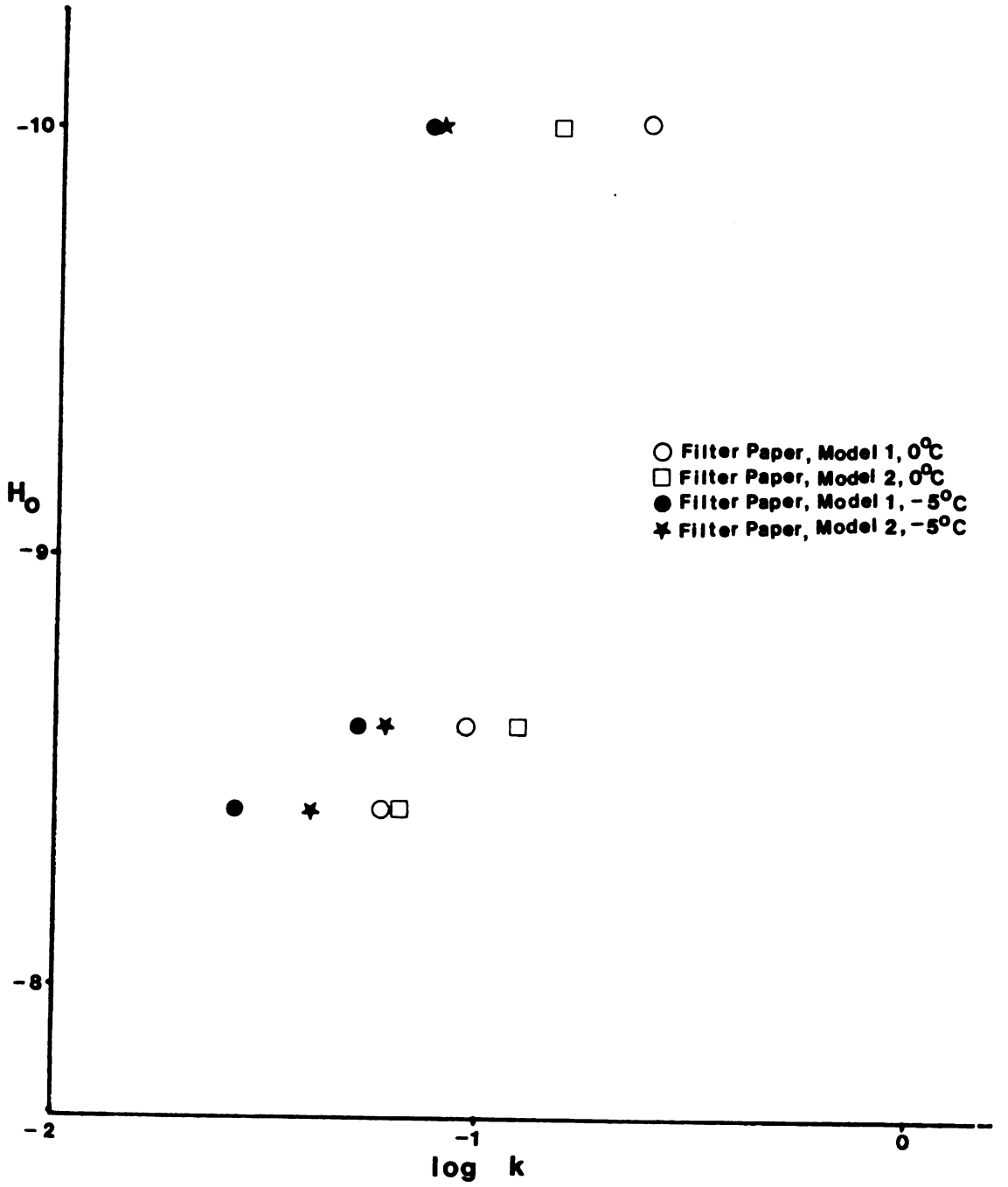


FIGURE 25

HAMMETT ACIDITY VS. LOG K

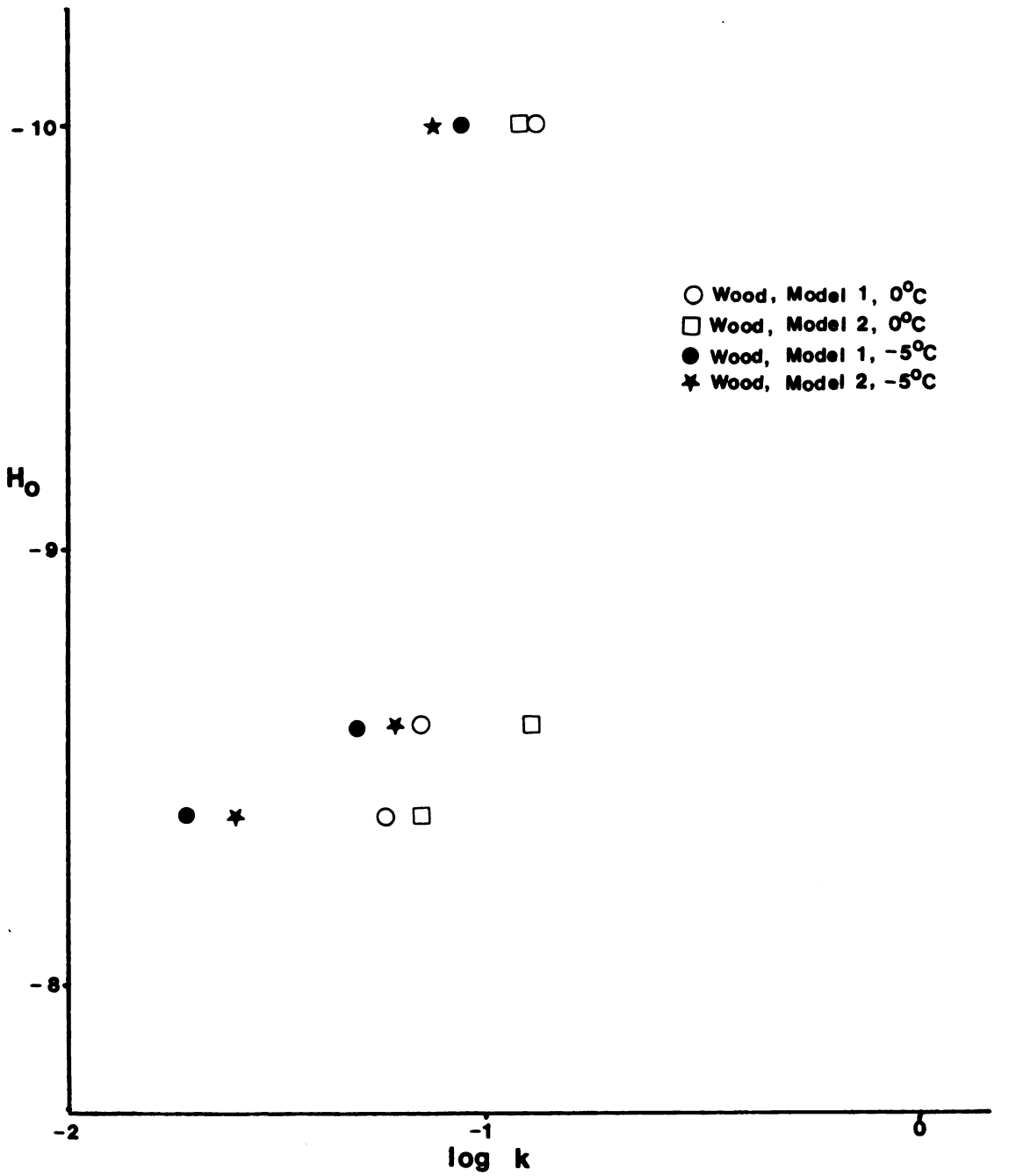


FIGURE 26

HAMMETT ACIDITY VS. LOG K

concentrations are lower than those calculated here, as these product solutions may contain a greater proportion of unreacted β-1-4 cellulosic linkages than do the products from warmer and more nearly anhydrous reactions. This would, of course, affect the relationship with the Hammett acidity function. However, this could cause a further departure from the predicted linear relationship with a slope of 1, rather than an improvement. To be closer to the predicted relationship, it would be necessary for the change in rate with water concentration between 3.6% and 6.4% water to be somewhat less than appears to be the case, and for the change to be very much greater between the 3.6% water and anhydrous cases.

B. XYLOSE

The kinetics of xylan saccharification were not examined in as much detail as glucan saccharification. In reactor design, a reaction time sufficient for reaction of cellulose will be more than sufficient for reaction of xylose, as xylan reacts much more quickly.

Two methods of data analysis were utilized for xylose production. In both, as with glucose, all soluble xylan was considered a reaction product. The first model was the simple least squares regression at an average reaction temperature as used for glucose. The data in Table 10 were obtained, with the fit to the model shown in Figures 27-29. The rate constants were generally calculated from the first few data points, as fluctuation about the final value was considerable in the middle and later periods. For this reason the correlation coefficients are not given, as they would appear misleadingly high. The gas chromatography analysis procedure itself is not as accurate for xylose as for glucose, probably due to the greater degradation of xylose during the derivatization procedure which must be corrected for with the response factor. In addition, the times selected for sample removal were oriented primarily toward examination of glucose kinetics, so were not always appropriate to xylan hydrolysis rates. The combination of these factors meant that rate constants for

TABLE 10

REACTION RATES FOR XYLOSE - MODEL 1

Substrate and conditions	Ave. T (^{o}C)	k_{-1} (min^{-1})	Initial delay (min)
Wood, anhydrous	3.9	.184	0.20
	-3.6	*	
	-8.2	*	
	-8.5	.084	0.29
Wood, 3.6% water	3.1	.157	0.29
	-9.1	.158	1.32
	-9.6	.151	0.62
	-10.6	*	
Wood, 6.4% water	2.5	.085	0.
	-6.2	*	
	-6.4	.097	(<0)

* No meaningful results

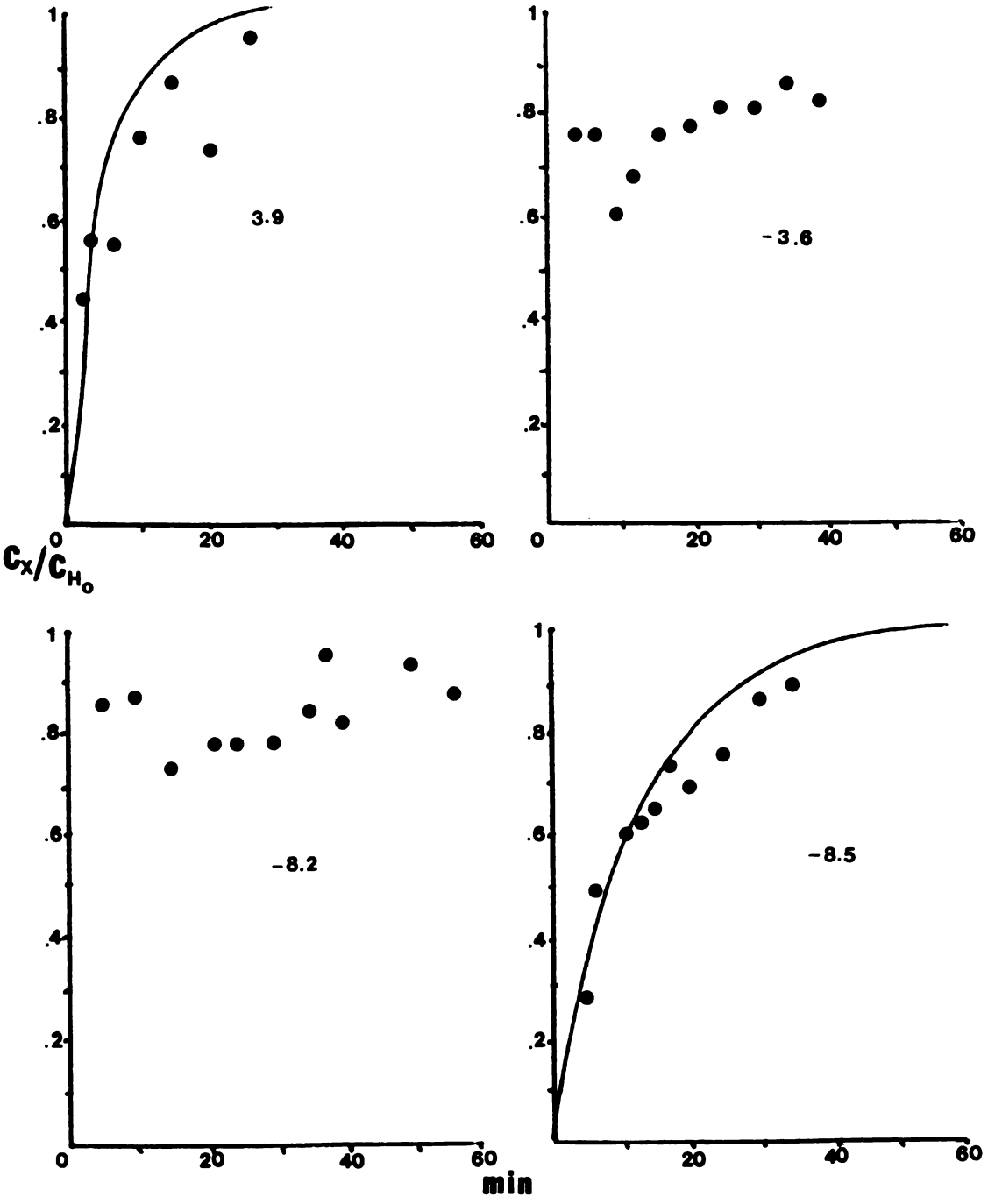


FIGURE 27

WOOD, ANHYDROUS HF - MODEL 1
(Conc. soluble xylan/initial conc. vs. time)

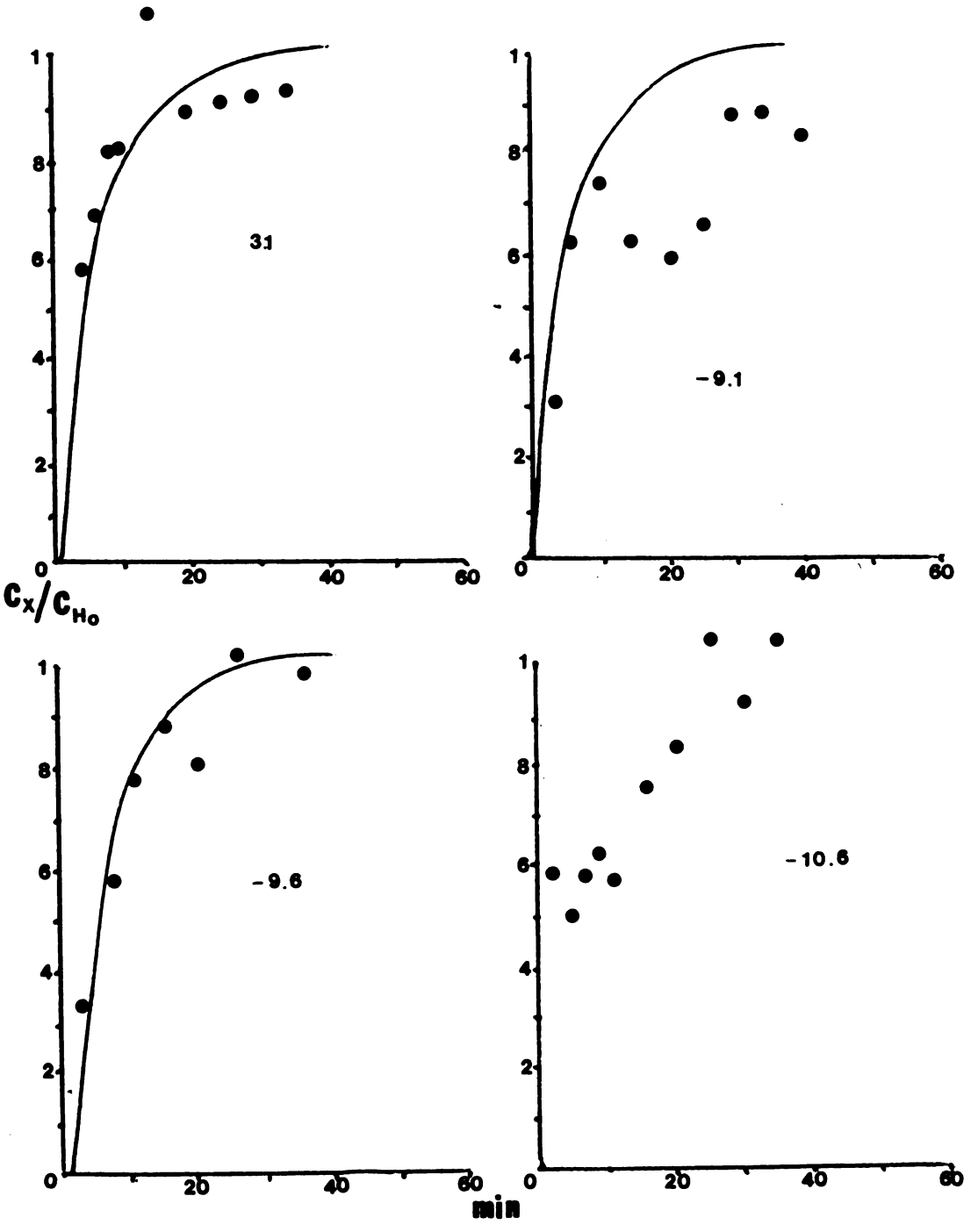


FIGURE 28

WOOD, HF WITH 3.6% WATER - MODEL 1
(Conc. soluble xylan/initial conc. vs. time)

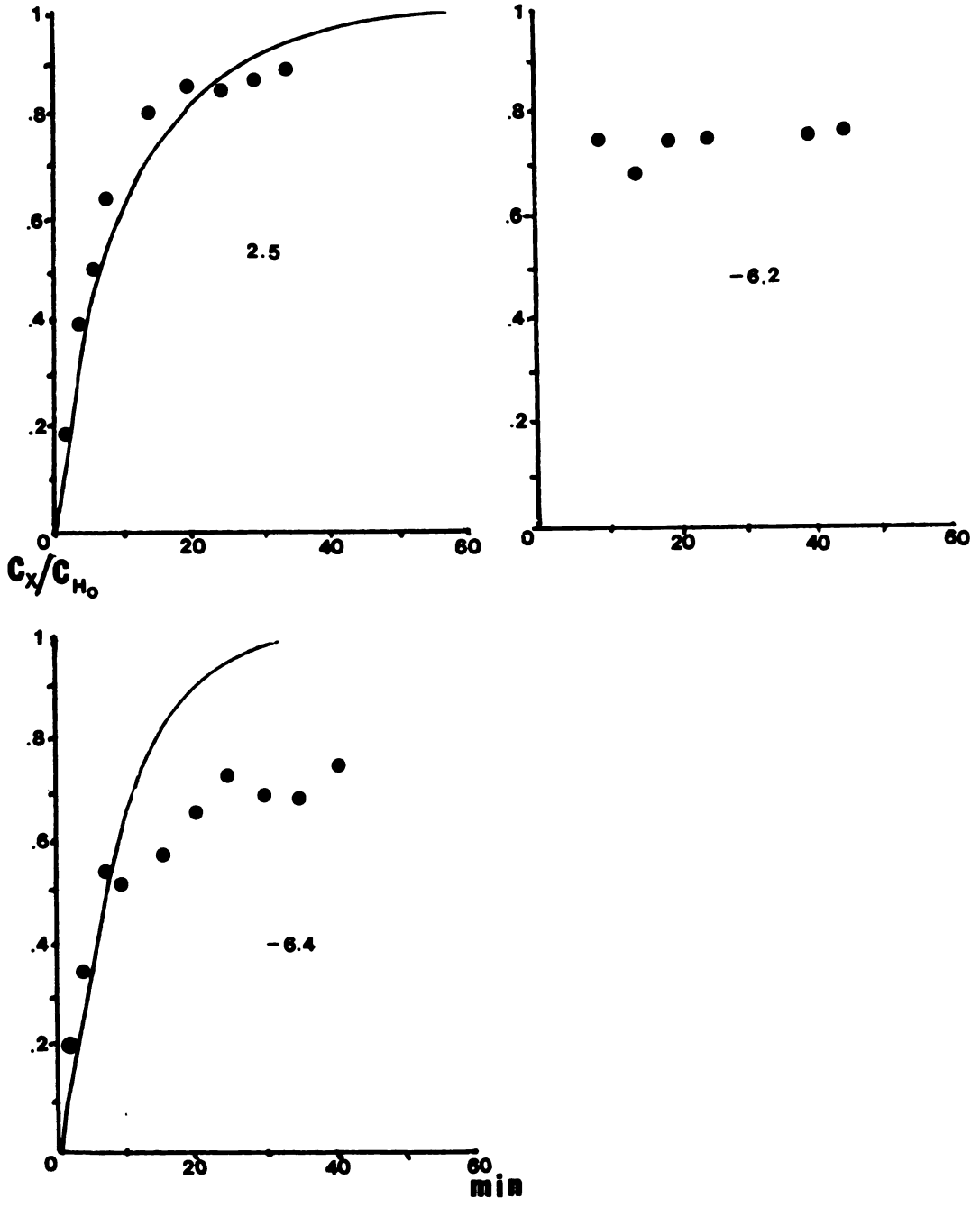


FIGURE 29

WOOD, HF WITH 6.4% WATER - MODEL 1
(Conc. soluble xylan/initial conc. vs. time)

xylose could not be obtained from all runs, as is indicated in the table.

As can be seen, this analysis was not very satisfactory, especially for the 3.6% and 6.4% water cases. The "initial delay" parameter was very small in all cases, making it reasonable to force the curve through the origin. Therefore the KINFIT4 program was used with concentration zero at time zero, and with the temperature fluctuations incorporated as they were for glucose. These results are presented in Table 11, with the corresponding curves in Figures 30-32. Calculated values for k at $0^{o}C$ and $-5^{o}C$ are presented in Table 12. As can be seen, it appears that the rates for anhydrous HF and for HF with 3.6% water are quite similar, as are the activation energies at these conditions. The rates at 6.4% water are slower for the two temperatures within the range of the data, though the higher (by 10 kcal) activation energy calculated leads to the prediction of a higher rate at $10^{o}C$, again probably a figment of extrapolation beyond the experimental range.

Because of the scatter in the data and its paucity, it would be unwise to draw many firm conclusions from these results. It does appear that an increase in water concentration has much less effect on xylan saccharification than on that of glucan, and that the activation energy is considerably less for xylan saccharification, at least

TABLE 11

REACTION RATES FOR XYLOSE - MODEL 2

Substrate	k at 10°C (min^{-1})	Std. dev.	E_a (kcal)	Std. dev.
Wood, anhydrous	.184	.060	6.5	3.1
Wood, 3.6% water	.162	.042	2.7	2.2
Wood, 6.4% water	.295	.091	16.5	3.5

TABLE 12

CALCULATED RATES FOR XYLOSE - MODEL 2

Substrate	0°C (min^{-1})	-5°C (min^{-1})
Wood, anhydrous	.121	.097
Wood, 3.6% water	.136	.124
Wood, 6.4% water	.101	.057

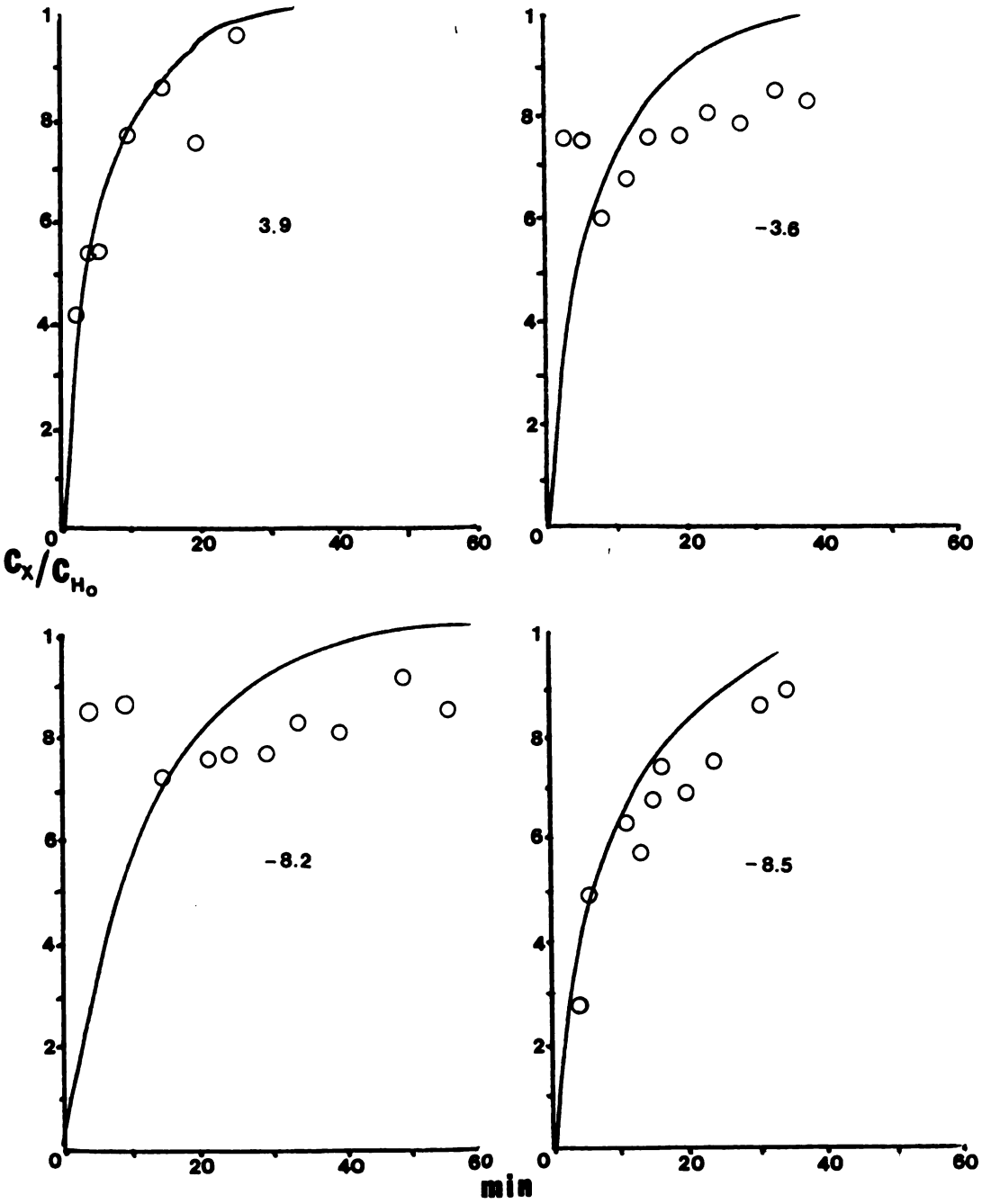


FIGURE 30

WOOD, ANHYDROUS HF - MODEL 2
(Conc. soluble xylan/initial conc. vs. time)

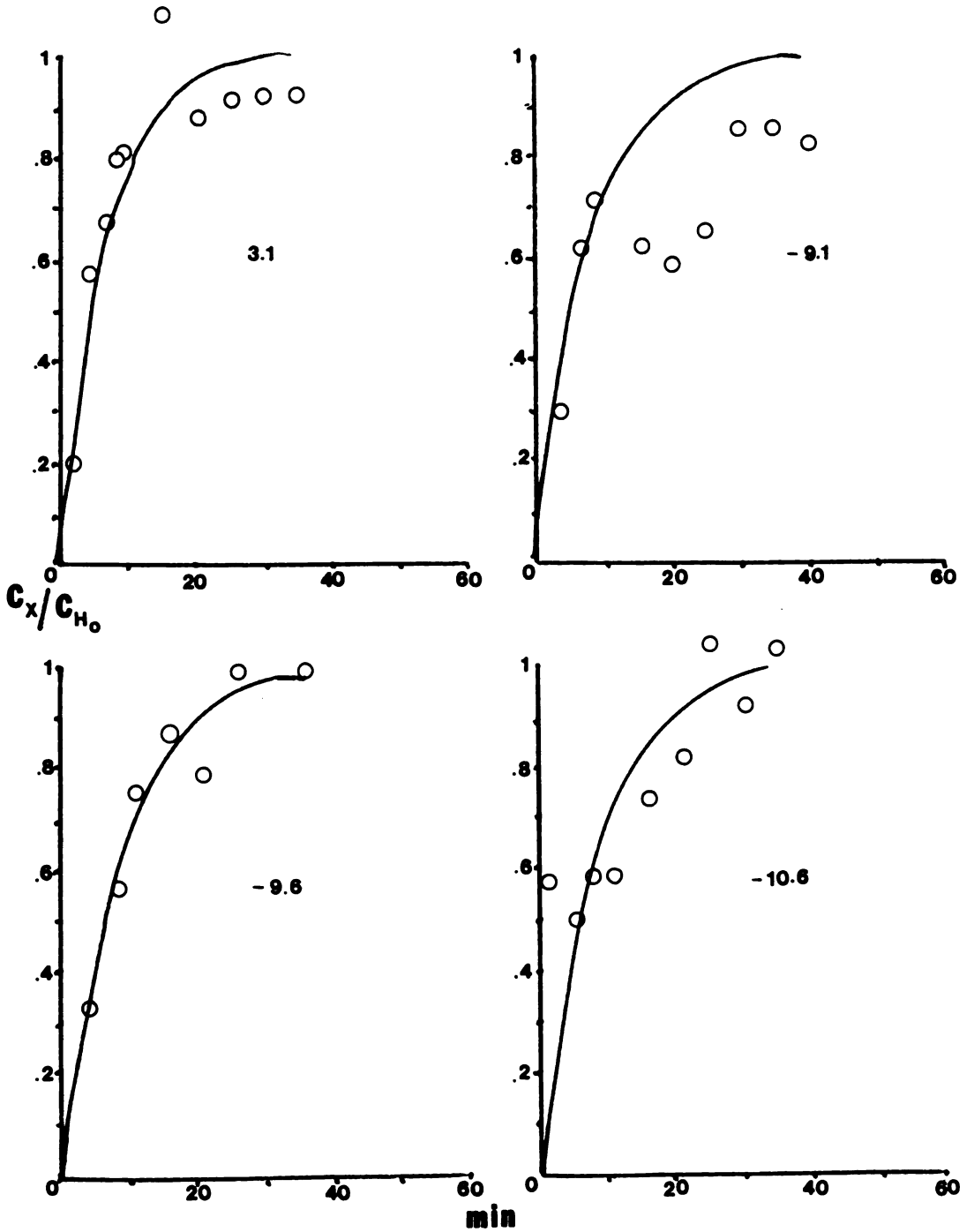


FIGURE 31

WOOD, HF WITH 3.6% WATER - MODEL 2
(Conc. soluble xylan/initial conc. vs. time)

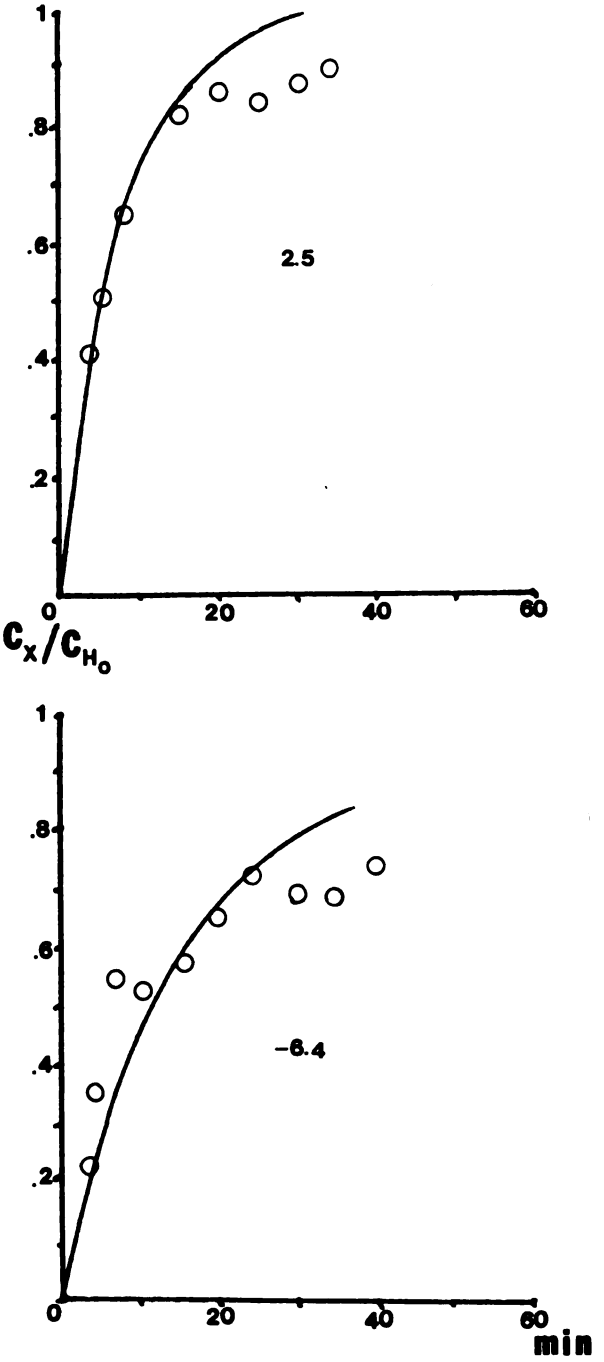


FIGURE 32

WOOD, HF WITH 6.4% WATER - MODEL 2
(Conc. soluble xylan/initial conc. vs. time)

at the two lower water concentrations. Further results must await experimentation directly designed to examine xylan reaction rates.

VIII. RESEARCH NEEDED

We have discussed elsewhere (Selke et al, 1982; Hawley et al, 1983) the advantages of HF saccharification over alternative hydrolysis technologies, and summarized these factors in Section I. However, if HF saccharification of lignocellulosic materials is to be justly evaluated in comparison to the alternative hydrolysis technologies, there is a considerable amount of further research required.

Extrapolation of the kinetic data presented here to a room temperature reaction presents the hazards always associated with extrapolation beyond the range of one's data, some of which were pointed out in the preceding section, where differences in calculated activation energies predicted a change in the relative sizes of rate constants at different water concentrations. This may be real or may simply be a function of experimental inaccuracies. The large marginal standard deviations in the consecutive reaction model mean predictions from that model cannot be made with a reasonable degree of accuracy for a room temperature reaction, though that is probably a more accurate and meaningful model than the ones with the artificial "initial delay" parameter. Thus there is a need

for further kinetic data, especially at temperatures likely to be of practical interest.

Selection of optimal water content for the feedstock will be influenced by the effect of water on the reaction rate, but within certain limits is likely to be more affected by the cost of drying the wood vs. cost of HF recycle, as the higher the HF:wood ratio, the larger the concentration of water in the feedstock for a given concentration of water in the HF. In addition, the effect of water concentration on HF removal and recycle must be taken into account, as well as the effect of water concentration on relative distribution of oligomers in the product.

The whole HF removal/recycle system has not yet been investigated. This may be a simple problem, but could hold some unexpected surprises. For instance, the effect of the biomass components on the vapor pressure of HF and of HF/water mixtures is not known.

The gas phase reaction may well be more economical than the liquid phase reaction due to lower HF requirements. If the correct kinetic model for liquid phase HF saccharification is dissolving of the cellulose followed by reaction with HF, the kinetics of the gas phase reaction would be expected to differ considerably from those of the liquid phase, as dissolving of the cellulose would not occur.

It was noted that acid hydrolysis rate constants tended to be species-dependent. This may also be the

case for HF saccharification, though in the sequential model the second rate constant is hypothesized to be independent of the source of the cellulose. In this model the species dependency would appear only in the first rate constant. In the initial delay models, the dependence could appear both in the initial delay parameter and in the rate constant. Investigation of a number of substrates will be required to clarify this dependence - which is known to exist for poplar wood and filter paper.

Another interesting area for further study is the product distribution from HF saccharification. This study looked only at total water-soluble sugars. As was discussed, examination of the sugar linkages is required to distinguish between reversion oligomers and partially hydrolyzed cellulose. Examination of these linkages and of the size distribution of the soluble oligomers formed should add considerable insight into the course of the reaction and its mechanism, and could also be valuable in specifying reaction conditions leading to a distribution of products suitable for various specific uses. For example, even if ethanol were the ultimate product goal, various enzyme systems can hydrolyze various types of sugar linkages in molecules of specific sizes at certain rates. Thus the choice of product from an HF saccharification reaction might depend on the enzyme system employed

to produce monomeric sugars from the sugar oligomers. Alternatively, a specified distribution of sugar oligomers might itself be the desired product.

Another major area for further study is the effect of particle size on the reaction kinetics. We have demonstrated that the reaction rate slows considerably in standard-sized wood chips (Selke et al, 1982), presumably due to mass transfer limitations. This effect must be investigated further in order to evaluate the relative costs and benefits of adding a particle size reduction step to the reaction concept. The choice of particle size will also have an effect on the economics of drying the substrate.

All of the above has not even considered the investigation of the lignin. Effect of various reaction conditions on the functionality of the lignin is a major study in its own right.

In summary, then, the major areas in need of further research are verification of the kinetic predictions at suitable operating conditions, investigation of HF:wood ratio effects, study of the HF removal/recycle system, investigation of the effects of particle size, product oligomer characterization, investigation of the gas phase reaction, which will again include many of the areas mentioned above plus basic kinetic data acquisition, and, finally, investigation of HF lignin. As can be seen, there is ample work still to be done.

IX. SUMMARY AND CONCLUSIONS

This investigation of HF saccharification had three major components: a survey of the literature on saccharification, development of a model for the reaction of HF with wood, and experimental determination of the effect of various reaction conditions on HF saccharification and determination of kinetic parameters for the reaction.

HF saccharification as a means of producing liquid fuels and chemical raw materials from biomass, a renewable substrate, has several advantages over existing acid and enzymatic hydrolysis technologies. These include high sugar yields with little or no degradation, short reaction times at essentially ambient conditions, efficient and relatively inexpensive acid recovery and recycle, chipping and drying as the only pretreatment requirements, no prehydrolysis requirement, and possible production of a valuable lignin byproduct.

Hydrolysis of cellulose by either dilute or concentrated acid is modeled as consecutive first-order reactions, first production of monomeric sugars and then decomposition of the sugars. The mechanism for glycosides is agreed to be protonation of a hemiacetal oxygen followed, in the rate-determining step, by bond fission to form the

conjugate acid and then fast reaction with water and loss of the proton to yield a sugar molecule. There is still debate about whether this mechanism yields a cyclic or acyclic intermediate, with the cyclic intermediate having the most support at present. The result of either mechanism is a dependence of the rate on the Hammett acidity of the medium and a difference in rate between non-reducing end linkages and those at the reducing end or internal to the molecule. Reaction rates in dilute acid are modeled as a rapid reaction of an initial portion of the material (the amorphous fraction) followed by a slow first order reaction of the remaining cellulose down to about 3% residue, at a rate 1-2 orders of magnitude less than for water-soluble glycosides. In concentrated acid the cellulose is considered to first dissolve and then hydrolyze. Reaction rates for wood are also modeled as first order. Rates are found to depend on the specific acid used and the cellulose type or wood species, as well as on the acid concentration in terms of the Hammett acidity. Activation energies are found to be about 28 kcal for cellulose and 40-44 kcal for wood. The mechanism of the solvolysis of glycosyl halides has been found to be similar to that of the acid hydrolysis of glycosides, and it has been suggested that the mechanism for HF saccharification of cellulose is also similar, though HF saccharification is not a

hydrolysis.

Enzymatic hydrolysis models are considerably more complex, as they must account for diffusion of enzymes into the structural matrix and adsorption and desorption of the enzymes along with product and substrate inhibition. No really successful model has yet been developed.

A model for HF saccharification was developed which treats all water-soluble oligosaccharides as reaction products. Mass transport within a wood chip is treated as two-dimensional with differing effective diffusivities in the longitudinal and transverse directions to account for the effect of the pore structure. Mass transport between the two phases is considered to be between a well-mixed bulk liquid and a particle surface with a film resistance. The low transverse diffusivity in the chip coupled with the low thickness to width ratio renders mass transfer through the lengthwise edge surfaces insignificant, reducing the problem to two dimensions.

Cellulose is divided into two types - crystalline and amorphous - with differing reactivities. Insoluble and HF-soluble glucans and xylans are differentiated from each other and from the water-soluble oligomers which are considered reaction products. Solid substrate can react directly to form products, or can form HF-soluble intermediates which then react further to form water-soluble products.

This model, though considerably simplified from the actual situation, contains a large number of unknown parameters, including time-dependent effective diffusivities, reaction rates, and mass transfer coefficients, and also requires coupled energy balance equations unless the particle and bulk fluid can be considered isothermal. Therefore the model is further simplified by reducing particle size to a point where mass and heat transfer resistances are insignificant. In addition the reaction scheme is simplified to solid glucan or xylan producing HF-soluble glucan or xylan which then react to produce water-soluble glucan or xylan, a simple sequential reaction, each part of which is hypothesized to be first order.

In the experimental work, the reaction of filter paper (pure cellulose) and of wood in a large volume of liquid HF was studied under anhydrous conditions, with HF containing 3.6% water by weight, and with HF containing 6.4% water. Temperatures studied ranged between -13 and 5^{o}C. The reactions were carried out in the presence of an internal standard which was carried throughout the gas chromatographic analysis procedures, and served to correct for variations in sample size as well as for sugar degradation during the analysis procedures and differential response of the sugars to derivatization, and for difference in the response of the detector to the various sugars in

the gas chromatographic analysis. Samples were removed from the reaction vessel at predetermined intervals, quenched in water, neutralized, the solid and liquid phases separated, and the liquid phase analyzed for total water-soluble sugars using a post-hydrolysis to convert all soluble oligomers to monomers followed by an alditol acetate derivatization and gas chromatography.

The data for water-soluble sugar yield as a function of time were analyzed utilizing several simple models. The first treated the reaction temperature as constant at the time-average value. Pseudo-first order rate constants and associated activation energies were determined for cellulose saccharification along with a required "initial delay" believed to represent time required for solubilization of the cellulose prior to reaction. The second model was similar except that the temperature variation during the reaction was considered explicitly. The third model, in accordance with the model developed for HF saccharification of wood, treated the process as two reactions occuring sequentially: first, solubilization of the cellulose in the HF, and second, reaction of the dissolved cellulose with HF to produce water-soluble products.

Several conclusions can be reached from this work. First, quantitative prediction of reaction times can now be made. For example, the reaction of anhydrous liquid

HF with small wood chips or smaller particles is essentially complete after 25 minutes at 4°C but takes about 50 minutes at -4°C and 70 minutes at -8°C. Therefore a reaction time of 10 minutes at room temperature should provide a sufficient safety margin to ensure complete reaction. For filter paper reaction is faster, requiring about 20 minutes at 0°C.

The presence of water significantly decreases the reaction rate. At 0°C for HF with 3.6% water about 25 minutes are required for complete reaction of filter paper and about 30 for complete reaction of wood at 3°C. At 6.4% water, reaction requires about 40 minutes for filter paper at 1°C and 35 minutes for wood at 3°C.

The reaction of HF with standard-sized wood chips is considerably slower, indicating that mass transfer plays an important role with this large particle size.

Activation energies obtained were 12-34 kcal/mole of sugar residue for the first-order models, with some tendency to be lower for wood than for filter paper. These activation energies are in the same range as those found for acid hydrolysis of cellulose, generally about 28 kcal/mole, but lower than those found for wood, about 40-44 kcal/mole.

It is important to realize that the rate constants and activation energies obtained do <u>not</u> represent a single

well-defined reaction, but rather represent the average of a number of reactions of a given type (see Section V).

As mentioned, the simple first-order model required the introduction of an "initial delay" parameter believed to be related to solubilization of the cellulose prior to or in conjunction with reaction. This parameter was particularly important at low temperatures, reaching as much as 24 minutes for filter paper with anhydrous HF at $-10^{o}C$. It decreased rapidly with increasing temperature and was near zero at temperatures of $0-5^{o}C$, so is likely to be zero for room temperature reactions at all the water concentrations studied.

The role of water in the reaction scheme is not clear. We know water is required for the production of sugars of low DP from cellulose, with one molecule of water required for each glycosidic linkage which is broken and does not recombine in the final product. The presence of water is also known to affect the Hammett acidity of HF, which is a measure of its proton-donating capacity. If the rate-determining step in HF saccharification is the formation of an oxocarbonium ion from a protonated glucan, as it is for acid hydrolysis, a linear relationship between the log of the rate constant and the Hammett acidity should be found. The relationship we find appears to be more complex than that, with a somewhat

larger decrease in rate between anhydrous and 3.6% water conditions than expected, and a considerably smaller decrease between 3.6% and 6.4% water than expected.

The sequential reaction model of solubilization of cellulose followed by reaction is more promising than the simpler pseudo-first order models, as it conforms more closely to the actual reaction sequence believed to occur. Unfortunately, determination of two rate constants plus two activation energies from only one measured quantity, total water-soluble sugars, leads to a very high degree of correlation between the parameters, making reliable determination of these parameters very difficult due to the very high marginal standard deviations obtained. Therefore a large amount of data of very high accuracy will be required, and/or experiments designed to separate these two reactions so that the rates can be measured independently. On a promising note, in the anhydrous case it was possible to combine the filter paper and wood reactions, considering the reaction rate of the dissolved cellulose to be independent of its substrate of origin.

In conjunction with this, it should be noted that analysis of total soluble sugars by the gas chromatographic procedure utilized led to a considerable amount of scatter in the results. Duplicate analyses of each sample were performed, and the difference in results from the two chromatographs was sometimes substantial (see Appendix 2).

This was especially the case for xylose, and is probably associated with degradation during the required post-hydrolysis. An analysis method which does not require extensive post-hydrolysis and derivatization should be more reliable and consistent.

There remains a large amount of work to be done before HF saccharification reaches the level of development of the competitive enzymatic and dilute acid hydrolysis processes. A kinetic study of room-temperature reactions is needed to extend the data in this study to more industrially useful conditions. Examination of the bond structure of the reaction products will provide more information about the intrinsic kinetics and help elucidate the reaction mechanism. It may also help explain the role of water in the reaction. Investigation of the reaction of HF with amorphous cellulose and separately with highly crystalline cellulose may enable the separation of contributions from these two types of cellulose in wood, and hence provide more accurate rate information.

The role of lignin in HF reaction should be further investigated. Lignin-sugar adduct formation is possible, and other effects on the reaction in addition to physical protection of the cellulose and enhancement of its crystallinity may occur.

In addition, the broad areas of lignin characterization

as a function of reaction conditions, optimization of HF recovery and recycle, investigation of the gas-phase reaction, and a survey of the reactivity of various substrates are all worthy of study. A major area for further investigation is the effect of particle size and the determination of the mass transfer properties of the system.

In conclusion, we believe that HF saccharification is potentially a highly efficient method for securing a renewable source of liquid fuels and chemicals, and therefore should be fully investigated.

APPENDICES

APPENDIX A

BIOMASS AVAILABILITY

Any process which envisions the use of wood or other lignocellulosic materials as a raw material for the production of liquid fuels and chemicals is dependent on the availability of the feedstock. This appendix will present a brief review of some of the research currently being done on biomass production and availability. It is not intended to be definitive, but merely to indicate the scope of the research being done.

A large number of articles have been written concerning the availability of wood and agricultural residues. Paul Risser estimated the total amount of available agricultural residues from 16 major agricultural crops as approximately 380×10^6 metric tons per year, and available wood residues as about 60×10^6 metric tons per year for the United States (Risser, 1981).

Ellis estimated above-ground residues one inch or larger in diameter left from the 1973 wood harvest as 110 million tons of wood and 20 million tons of bark on an oven dry basis, with an additional 10 million tons of wood and 7 million tons of bark as unused residues from primary wood processing (Ellis, 1976).

Other investigators have focused on increasing the amount of wood harvested from the nation's forests, usually using whole-tree chipping. According to Stone (1976), in 1970 the net forest growth on commercial forest land was 18.6 billion cubic feet, 30% above that year's harvest. He stated that the rate of timber growth is accelerating, having risen 14% between 1960 and 1970, but was still only about half the potential growth of fully stocked stands. His figure for wood residues left in the forest in 1973 was the same as that of Ellis. In addition, he stated that about 33 million tons of potentially recyclable waste paper was not recycled or otherwise utilized.

Burwell (1978) quoted a National Research Council estimate that forest yields could be doubled if the forests were subjected to improved management.

Some studies have focused on specific states or areas. Frederick (1979) estimated that 20% of the Southeastern states' energy needs could be supplied from wood without hurting the area's wood-using industries. Deal (1981) estimated that about 14.4 million green tons per year were currently available for new markets at a cost of $14-$18 per green ton for the chips, in the same area. This figure was reduced from 31.4 million by considering limitations of location, harvesting technology, and costs.

Mattson and coworkers (Mattson et al, 1978) estimated that for good forest management about 40 million green tons

of wood per year should be harvested from 18 million acres of commercial forest land in northern Wisconsin and the Michigan upper peninsula, about 8 times the current harvest. About half that amount was tops, limbs, and rough and rotten trees. They estimated that after excluding saw logs, over 30 million green tons would be available for fiber or fuel at an average delivered cost of less than $15 per green ton. On a national basis, they quoted a USDA Forest Service estimate in 1978 that over 146 million dry tons of wood was available in the eastern United States if all cull sections, tops, and limbs from cut trees and all rough, rotten and dead trees were removed from logged areas. This does not include wood available from areas needing thinning or other improvement cuts or from mature stands not being harvested.

Another source of wood is from silviculture energy farms. Dawson (1978) estimates that under a short rotation intensive culture system, a Populus hybrid can produce 15.2 metric tons per hectare per year, compared to 5.26 for a natural stand of aspen. Henry (1981) presents production estimates for several varieties of trees in an energy farm style of cultivation. His estimate for poplar is 2-8.5 oven-dry tons per acre per year. In an economic evaluation of a 250,000 ODT/year energy farm with a productivity of 5-12 ODT/acre year (and therefore a size of 50,000 to 21,000 acres) utilizing fast-growing hardwood on a 6 year

rotation, he estimated production costs of $34.73/ODT for Wisconsin and $23.53/ODT for Louisiana. His computed ratio for energy in to energy out was 1:10.6 for Wisconsin and 1:15.3 for Louisiana.

Other novel approaches to energy farming have included a proposal to use sewage and a fraction of a municipal waste stream as fertilizer for an energy plantation (Stanford, 1979).

One of the disadvantages of biomass as a feedstock is its bulk, leading to high transportation costs. One investigator (Rich, 1981) has suggested a harvest radius of approximately 50 miles as the maximum for biomass considering the present cost of competitive fuels. Densification of wood has been suggested to reduce transportation costs (Reed and Bryant, 1978a, 1978b).

Thus it can be seen that in at least some areas of the country there is currently a considerable amount of biomass, either trees or agricultural residues, which is not currently being utilized. Applying scientific management practices to existing forest lands can considerably improve their productivity, adding to the biomass supply. In addition, the planting and cultivation of energy plantations can provide further sources of wood. Thus biomass in general and wood in particular does have the potential to be a significant source of material for fuel and chemical production.

APPENDIX B

REACTION DATA

Filter paper, anhydrous HF, average temperature 1.3°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
1		1.335
		1.066
2	3.2	.590
		.630
4	2.6	2.598
		2.417
8	1.6	5.831
10	1.2	5.745
		5.663
12	1.0	5.449
		5.354
15	0.7	6.420
		5.473
20	0.5	5.872
		6.505
25	0.4	5.475
		6.238

Filter paper, anhydrous HF, average temp. -1.9°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
3	-1.0	.259
		.585
6	-2.1	2.208
		2.210
10	-2.7	4.933
		4.963
15	-2.8	6.784
		6.441
21	-2.7	6.679
		6.255
25	-2.9	6.374
30	-2.7	6.188
		6.319
35	-3.3	6.552
		6.118
40	-3.4	6.142
45	-3.3	6.066

Filter paper, anhydrous HF, average temp. -9.5°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
5	-8.6	.087 .076
10	-8.0	.226 .092
15	-9.7	.761 .439
20	-11.2	1.493
25	-10.9	2.319 2.234
30.2	-10.4	3.014 2.844
35	-10.7	2.871 3.086
40	-10.5	3.675 3.507
50	-8.5	4.304 4.112
60	-7.2	6.065 6.215

Filter paper, anhydrous HF, average temp. -11.9°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
4	-11.1	.093
6	-11.2	.037
8	-11.2	.033
10	-11.0	.032
15	-11.0	.051 .062
20	-12.9	.145 .233
25	-12.8	.341 .486
33	-10.1	1.352 .940

Filter paper, HF with 3.6% water, ave. temp. 1.4°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
4	1.7	2.857 3.175
6	1.5	2.114 2.278
8	1.3	2.520 2.353
10	1.2	3.351 3.452
15	1.1	4.598 4.926
20	1.1	6.324 6.449
25	1.3	6.023 5.722
30	1.5	6.001 6.320
35	1.5	6.266 6.093

Filter paper, HF with 3.6% water, ave. temp. 0.3°C*

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
2	1.4	.311 .246
4	1.0	.564 .792
6	.7	1.372 1.415
8	.5	1.988 2.023
10	.4	2.908 2.898
15	.2	4.563 4.597
20	.15	5.783 6.174
25	.1	7.240 7.221
30	.1	7.478 5.771
40	.1	7.796 7.320

* C_{C_o} adjusted to 7.2

Filter paper, HF with 3.6% water, ave. temp. -7.4°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
2	-5.9	.082
		.066
4	-6.5	.067
		.087
7	-7.0	.061
		.067
10	-7.2	.096
		.142
15	-7.3	.124
		.190
20	-6.6	.809
		.991
25	-6.9	1.849
		2.306
30	-9.0	3.221
		2.815
35	-9.0	3.566
		3.783
40	-8.2	3.944
		3.759

Filter paper, HF with 3.6% water, ave. temp. -9.0°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
2	-13.2	0
		.168
4	-12.8	.178
		.234
6	-12.2	.080
		.094
8	-11.8	.151
		.119
10	-11.3	.207
		.183
15	-9.8	.556
		.460
20	-8.8	.600
		.789
25	-8.0	1.638
		1.727
30	-6.5	1.479
		1.536
40	-4.8	3.045
		2.933

Filter paper, HF with 6.4% water, Ave. temp. 1.3°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
4	.7	.299
		.373
6	.5	1.041
		1.073
8	.6	1.106
		1.314
10	.7	2.655
		2.686
15	.9	2.863
		3.315
20	1.1	4.821
		5.292
25	1.5	5.156
		5.333
30	2.0	6.396
		6.364
35	2.4	6.970
		6.961
40	2.2	7.576
		7.601

Filter paper, HF with 6.4% water, Ave. temp. -6.0°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
2	-9.6	.147
		.117
10	-8.5	.653
		.666
26	-5.3	1.243
		1.056
30	-3.8	1.661
		1.593
36	-1.9	2.363
		2.094
40	- .8	2.682
		2.665

Filter paper, HF with 6.4% water, ave. temp. -7.2°C

Time (min)	Temperature (°C)	Soluble glucan (m x 10^3/g)
2	-6.4	.079
		.102
4	-6.6	.149
7	-6.9	.298
10	-7.1	.455
		.445
15	-7.2	1.945
		1.677
20	-6.4	1.575
		1.513
25	-6.5	2.585
		2.304
30	-7.7	3.043
		2.693
40	-8.4	4.456
		3.961
50	-7.6	5.248
		5.566

Wood, anhydrous HF, average temperature 3.9°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
2	3.1	.648	.532
4	3.0	1.137	1.143
		.434	.661
6	3.0	.757	1.901
		.763	1.804
10	3.2	1.119	3.049
		1.003	2.798
15	3.7	1.355	3.139
		1.068	2.902
20	4.3	1.109	3.411
		.935	2.988
26	4.4	1.348	3.873
35	4.7	1.249	3.189
		1.102	3.029

Wood, anhydrous HF, average temperature -3.6°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan
4	-2.2	1.024	.667
		1.115	.453
7	-1.7	1.087	.744
		1.044	.951
10	-2.2	.826	.772
13	-3.1	.886	1.218
		1.016	1.428
16	-3.7	1.074	1.685
		1.066	1.763
20	-4.1	1.060	2.145
		1.088	2.198
25	-3.9	1.171	2.717
		1.093	2.707
30	-4.4	1.056	2.913
		1.133	2.987
35	-5.0	1.161	3.177
		1.233	3.280
40	-5.1	1.130	3.240
		-	3.140

Wood, anhydrous HF, average temperature -8.2°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
5	-11.2	1.141	.254
		1.270	.241
10	-10.4	1.343	.289
		1.228	.250
15	-8.5	.945	.417
		1.074	.502
21	-6.1	1.077	.833
		1.054	.857
25	-4.6	1.053	1.651
		1.079	1.591
30	-6.8	1.013	2.352
		1.145	2.506
35	-8.8	1.160	2.894
		-	2.983
40	-9.3	1.140	2.891
		1.137	2.874
50	-8.1	1.155	3.021
		1.463	3.092
57	-4.7	.971	2.495
		-	3.026

Wood, anhydrous HF, average temperature -8.5°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
5	-8.5	.335	.199
		.434	.368
7	-8.4	.757	.149
		.606	.199
11.5	-6.5	.815	.266
		.858	.312
13	-6.2	.739	.831
		-	.841
15	-8.2	.917	.938
		.912	.944
17	-9.8	.885	.868
		-	.976
20	-10.9	.949	1.136
		.947	1.059
25	-10.8	1.022	1.302
		1.027	1.268
30	-8.6	1.091	1.958
		-	2.133
35	-6.0	1.172	2.758
		-	2.884

Wood, HF with 3.6% water, average temperature 3.1°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
2	2.4	.297	.187
		-	.253
4	2.9	.867	.486
		.803	.404
6	2.7	.933	.675
		1.025	.744
8	2.6	1.153	1.221
		-	1.371
10	2.6	1.173	2.064
15	3.0	1.623	3.656
		1.430	3.477
20	3.1	1.192	3.153
		1.274	3.229
25	3.3	1.377	3.382
		1.156	2.992
30	3.6	1.287	3.276
35	3.8	1.298	3.345
		1.265	3.340

Wood, HF with 3.6% water, average temperature -9.1°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
4	-8.3	.642	.133
		.255	.105
7	-8.6	.866	.246
10	-8.7	1.078	.390
		.995	.358
15.1	-8.6	.861	1.750
20	-8.0	.590	.557
		1.049	.764
25	-9.5	.958	2.650
		.811	3.510
30	-10.3	1.239	2.220
		1.153	2.187
35	-10.4	1.140	1.590
		1.218	1.544
40	-9.8	1.150	2.030
		1.147	2.251

Wood, HF with 3.6% water, average temperature -9.6°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
1	-9.0	.286	.079
		.187	.044
3	-9.4	.482	.257
		.416	.291
7	-9.8	.853	.156
		.760	.101
10	-9.5	1.037	.202
		1.135	.231
15	-8.6	1.288	.455
		1.190	.419
20	-10.1	1.112	1.901
		1.105	1.940
25	-11.3	1.432	1.640
		1.417	1.765
35	-7.3	1.355	2.058
		1.413	2.003

Wood, HF with 3.6% water, average temperature -10.6°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
2	-10.6	.815	.125
		.821	.139
4	-11.3	.461	.108
		.977	.162
6	-11.6	.773	.147
		.827	.205
8	-11.6	.753	.137
		-	.175
10	-11.3	.698	.133
		-	.174
15	-9.6	.893	.368
		1.175	.515
20	-10.8	1.051	1.024
		1.265	1.244
25	-11.2	1.506	1.677
		1.004	1.486
30	-9.8	1.171	1.605
		-	1.881
35		-	1.615
		-	1.834

Wood, HF with 6.4% water, average temperature 2.5°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan ($m \times 10^3/g$)
4	1.6	.617	.416
		.641	.527
6	1.4	.783	1.110
		.818	1.095
8	1.3	1.048	1.777
		1.036	1.837
15	2.2	1.230	2.007
		1.354	2.088
20	2.7	1.351	2.560
		1.388	2.486
25	3.2	1.371	3.101
		1.284	3.042
30	3.7	1.433	3.467
		1.348	3.274
35	4.1	1.429	3.570
		1.377	3.409

Wood, HF with 6.4% water, average temperature -6.2°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan
3	-9.1	-	.398
		-	.316
5	-9.0	-	.293
		-	.269
10	-7.4	.999	.420
		1.097	.318
30	-5.0	1.207	.543
		1.345	.555
35	-5.0	1.414	.689
		1.530	.602
40	-5.4	1.005	.816
		1.029	.756
45	-5.0	1.051	1.934
		1.060	2.018

Wood, HF with 6.4% water, average temperature -6.4°C

Time (min)	Temperature (°C)	Soluble xylan ($m \times 10^3/g$)	Soluble glucan
2	-4.4	.303	.071
		.319	.055
4	-4.5	.490	.112
7.5	-4.3	.762	.195
10	-4.0	.754	.338
		.685	.381
15.5	-6.6	.937	.699
		.707	.644
20	-7.8	.864	.722
		.983	.766
25	-8.3	.939	.775
		1.047	.741
30	-7.9	.996	.918
		.923	.919
35	-7.1	.977	1.224
		.923	1.255
40	-6.1	.987	1.663
		1.078	1.704

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