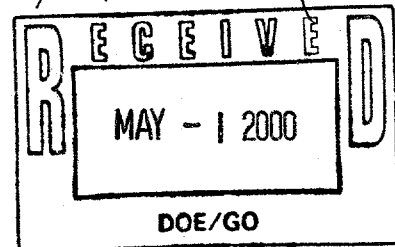


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**Enhancement of Dilute-Acid Total-Hydrolysis Process for
High-Yield Saccharification of Cellulosic Biomass**

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Task I. Kinetics of Cellulose Hydrolysis under Extremely-Low-Acid and High Temperature Condition

A. Insights on Reaction Mechanism of Acid Hydrolysis Cellulose

In order to assess the current situation of the kinetic investigation in our project, we have given further thoughts on this issue and performed detailed analysis of literature information. Some of these efforts are summarized here.

The principal molecular mechanism of acid hydrolysis, which was confirmed by model and tracer studies, is outlined in following Figure¹. Acid hydrolysis, leading finally to a fission of glycosidic bonds, proceeds in three steps. The reaction starts with a proton of catalyzing acid interacting rapidly with the glycosidic oxygen linking two sugar units (I), forming a so-called conjugate acid (II). The next step is the cleavage of the C-O bond and breakdown the conjugate acid to the cyclic carbonium ion, which adopts a half-chair conformation. After a rapid addition of water, free sugar and proton is liberated²⁻⁵. The formation of the intermediate carbonium ion then takes place more rapidly at the end than in the middle of the polysaccharide chain. In accordance with this, the yield of monosaccharides after partial hydrolysis is higher than that calculated on the basis of a

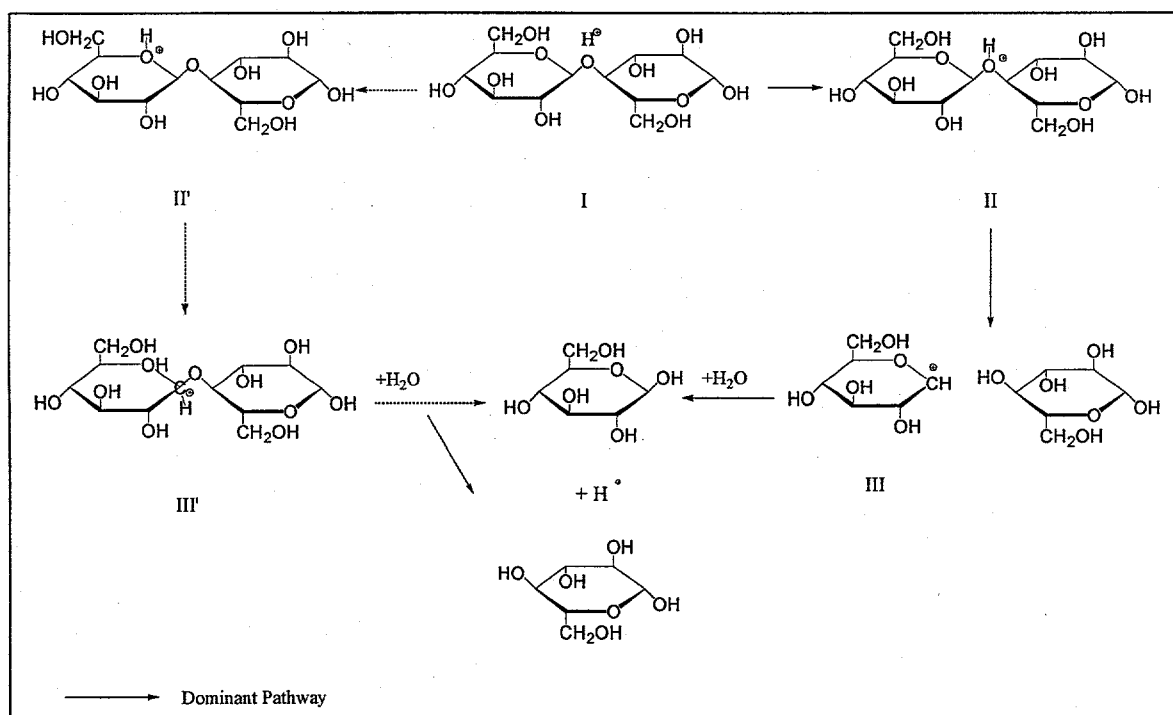


Figure 1. Mechanism of acidic hydrolysis of glycosidic linkages

random bond cleavage.

Because the sugar molecules compete with the solvent (water), small amounts of disaccharides are formed as reversion products in concentrated solutions⁶. Reversion tends to result in formation of (1→6-) glycosidic bond. Acid can also catalyze the dehydration reaction of hydrolyzed sugars. Depending on the acid concentration and the temperature, numerous reaction products are possible, most of them being rather unstable or formed only in very low concentrations^{4,7-8}. The acid-catalyzed dehydration under mild conditions leads to the formation of anhydro sugars with intramolecular glycosidic linkage, resulting from the elimination of a water molecule from two hydroxyl groups. As these glycosidic linkages can easily be hydrolyzed, a series of further degradation products may be formed. Some of them are aromatic and condensed compounds (see figure 2). The degradation of pentoses and uronic acids into furfural and of hexoses into hydroxymethylfurfural, levulinic acid and formic acid are the major degradation reactions. These reactions occur primarily under concentrated acid and higher temperatures^{4,9}.

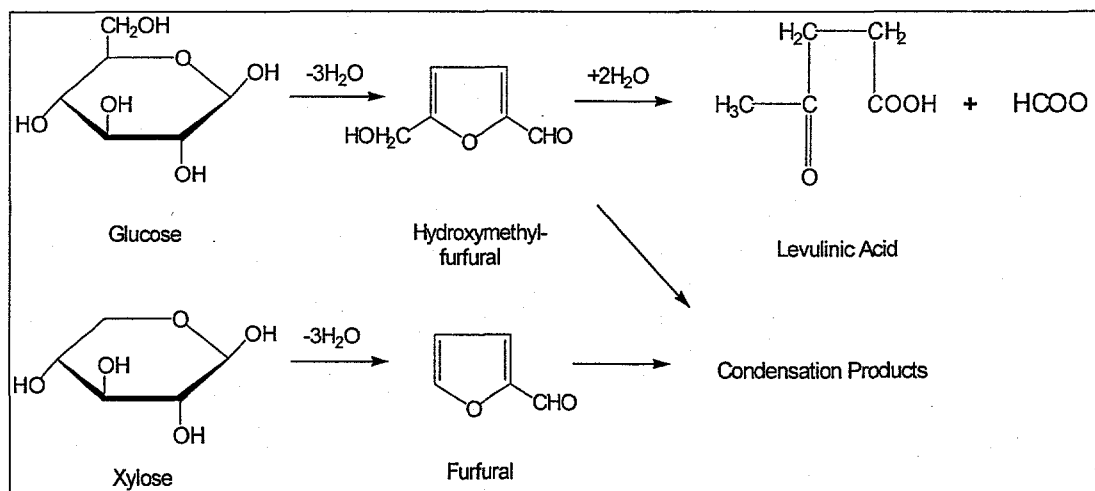


Figure 2. Formation of furfural, hydroxymethylfurfural, levulinic acid and formic acid from monosaccharides in acidic medium¹

Factors Influencing Acid Hydrolysis

Although the principles of cleaving glycosidic linkages by acid-catalyzed reaction are generally valid, the special kinetic data and the overall course of degradation are influenced both by the applied acidic medium and the characteristics of the cellulose. The hydrolyzing medium can be characterized by:

- kind of acid
- acid concentration and ion strength
- pH value
- temperature and pressure.

With regard to the cellulose, important factors are:

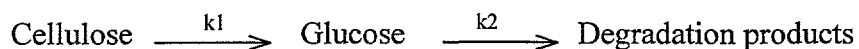
- phase state
- physical structure and accessibility in the case of heterogeneous hydrolysis
- conformation effects
- ring structure and substituents⁶.

Acids are characterized by their acid strength values (pKa value). Also the hydrolytic activity (expressed by the pH value) and the activation coefficient of the hydronium ion (expressed by the Hammett acidity function) influence the overall hydrolysis rate of glycosidic linkages. Additional parameters are temperature and pressure. Generally, increased temperature and pressure accelerate the hydrolysis velocity to some extent, depending on the special acid characteristics mentioned above¹⁰.

High yield and reaction rate of glucose is not attained simply by removal of lignin and hemicellulose formation from cellulose. Even cellulosic materials that never had lignin and hemicellulose associated with them (e.g. cotton) are difficult to hydrolyze without pretreatment¹¹⁻¹². Because cellulose consists of regions of high and relatively low crystallinity, acid hydrolysis processes to disrupt cellulose operate at two different levels: inter-crystalline and intra-crystalline. The conditions required is relatively mild to swell low crystalline regions (e.g. amorphous cellulose), where drastic processes are required to affect the high-crystalline regions. This generate a major problem for acid hydrolysis that amorphous cellulose goes rapidly through glucose to degradation products, while crystalline cellulose takes time to convert to a readily hydrolyzed form¹¹.

Kinetics and Model of Dilute Acid Cellulose Hydrolysis

The initial kinetic study of cellulose hydrolysis was by Saeman¹³. From experiments using Douglas fir in a batch reactor, dilute acid hydrolysis was described using two pseudo-homogeneous consecutive first order reactions.



Hydrolysis of glycosidic bonds usually follows a first-order reaction¹⁴⁻¹⁵. The individual hydrolysis rate depends on the parameters of the acid and the sample. The reaction rate equations describing cellulose and glucose concentrations are:

$$\frac{dC}{dt} = -k_1 \cdot C \quad \frac{dG}{dt} = k_2 \cdot G - k_1 \cdot C$$

for which the reaction rate constants follow an Arrhenius temperature dependence of the form:

$$k_i = k_{i0} \cdot A^{m_i} \cdot e^{(-E_i/RT)}$$

k_{i0} is the pre-exponential factor, A is the concentration of acid (wt %), m_i is a power, and E_i is the activation energy. These four parameters are determined experimentally and were found to vary with substrate. Glucose yield, the focus of most hydrolysis studies, is evaluated by the following integrated equation:

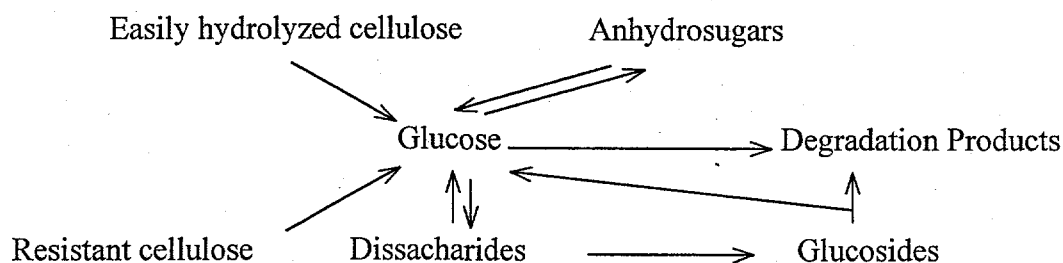
$$G = C_0 \left[\frac{K_1}{K_1 - K_2} \right] \cdot (e^{-K_2 t} - e^{-K_1 t}) + G_0 \cdot e^{-K_2 t}$$

in which G is the fraction of the total potential glucose as glucose and C_0 and G_0 are the initial fractions of potential cellulose and glucose, respectively.

These kinetic equations are generally used to elucidate reactions in homogeneous phase. Therefore, in exact sense, they apply only to glycosides, di-, oligo- and those polysaccharides which are readily and totally soluble in the hydrolyzing medium. A totally heterogeneous reaction takes place in the case of partial hydrolysis with highly diluted acids, yielding so-called hydrocellulose, a product with reduced DP but higher crystallinity¹⁶. The rate of heterogeneous hydrolysis of celluloses, which are 1-2 orders of magnitude less than those of homogeneous hydrolysis of model compounds, are mainly influenced by the degree of crystallinity and the swelling state of cellulose. Both characteristics can be influenced by mechanical disintegration and/or decrystallization procedures^{5,17}.

There have been several improvements to the kinetic model originally suggested by Saeman¹³. It is obvious that this model is missing an important factor for the more easily hydrolyzed amorphous cellulose. The amorphous cellulose hydrolyzes almost instantaneously to glucose, an initial glucose concentration must be assumed. The more

extended model was suggested by Conner et al. upon the study of the reversion reactions of glucose¹⁸:



Implementation of the modified kinetic model, such as inclusion of the reversion reactions, the fit of experimental data to the predicted model can be improved.

B. Experimental Kinetic Study

The primary emphasis of the project work during this period was placed on the Task I. Upon completion of the design and construction of the experimental set-up (previously reported), the batch kinetic experiments were conducted. The initial series of experiments were done with α -cellulose using batch reactors. Taking this as the basis cases, similar experiments were then carried out using untreated and pretreated Yellow Poplar feedstocks. The batch kinetic experiments were conducted with 0.07% H_2SO_4 , and at three different temperature of 205, 220, and 235°C. The results are summarized in attached Tables 1 & 2 and Figures 9 & 10.

We have also constructed a bed-shrinking flow-through reactor system that NREL has invented. Some of the reactor parts and temperature control system was loaned out from NREL for this study. An important series of experiments were performed for a kinetic study on the yellow poplar feedstock using this reactor system. In our experiments using the flow-through reactor, we have followed the time course of solid and liquid composition and the terminal yields. Three different temperatures of 205, 220, and 235°C were applied. The results are summarized in attached Table 3 and Figure 11.

The major findings in the batch and flow-through reactor experiments are as follows:

1. In Batch reaction, the maximum yield of glucose from α -cellulose is about 60% for 205 and 220°C. However, the maximum yield at 235°C is substantially lower at 40%. It is contrary to the conventional concept of cellulose hydrolysis where higher yields are obtained at higher temperature because the activation energy for hydrolysis higher from the hydrolysis than the decomposition reaction. The reason is unclear at this time whether the results reflect the true kinetic behavior or the maximum point in the data was somehow missed in our experiments because the reaction occurs rapidly, the maximum point occurring at about ten-minute point. Other side reactions may also occur at 230C.
2. The maximum yield of glucose from yellow poplar is much lower than that from α -cellulose over the entire range of experimental batch reaction conditions. The difference was most significant at 205C where the maximum observed batch yield is only 30% for the untreated and pretreated yellow poplar feedstocks.
3. The glucan decay in the solid substrate in batch experiments is rather insensitive to the temperature over the experimental range applied in this study (205 –235°C). See the semi-log plot of Fig. 9, 10 & 11. Again this is a drastic departure of the known kinetics of cellulose hydrolysis at higher acid concentrations (above 0.5%).
4. We have confirmed the earlier research work of NREL that the bed-shrinking flow-through reactor (percolation reactor) provides glucose yield in the vicinity of 90%. We have obtained yields of 87.54%, 90.32%, and 90.78% respectively at 205, 220, and 230°C.

Follow up experiments are being conducted for confirmation and verification of these findings. The issues being addressed in the follow up experiments are the difference in the yields between the two reactor types and the difference between the two substrates. These are crucial items in the hydrolysis of cellulose by the extremely dilute acid. We are

reporting on the reassessment of the kinetic background of the cellulose hydrolysis and a part of the follow up experiments.

Additional Observations from the Batch Experimental Data

The current models for acid hydrolysis of cellulose predict that glucose yields higher than 70% are not attainable. Conner et al.¹⁹ suggested that once glucose is formed under reaction conditions, it can derivatize and/or degrade via oxidation reactions or polymerization reactions. Bouchard et al.²⁰ suggested that only about 60-70% of the theoretical glucose yield from cellulose can be obtained because the cellulose is chemically altered after about 70% conversion. Therefore, the resulting solid substrates are not quantitated as cellulose and can no longer be hydrolyzed to release glucose. Mok and Antal²¹ suggested that about 30% of the hydrolyzed cellulose gives rise to oligomers, which cannot be converted to glucose either at reaction temperature or after traditional post-hydrolysis conditions using 4% sulfuric acid. However, recent work at the National Renewable Energy Laboratory (NREL) on the aqueous fractionation of yellow poplar using a simulated countercurrent reactor system has produced glucose yields higher than 85%²² using 0.07% w/w sulfuric acid and 225°C. The same results have been reproduced in our laboratory. These results are contradictory to the previously published cellulose hydrolysis kinetic models. The kinetics on fractionation of glucose from hardwood cellulose using dilute sulfuric acid needs to be readdressed.

To study the kinetic sequences in hardwood (yellow poplar) cellulose hydrolysis, a traditional semilog plot of cellulose disappearance as a function of hydrolysis time was used. Although all published kinetic curves studying hardwood cellulose hydrolysis use batch ampule reactors and acid concentrations of about 0.4-1.6 wt% sulfuric acid, we have used traditional batch reactors and a flow-percolation reactors as previously describe. It has been confirmed that a continual shrinking bed reactor can produce glucose yields of 86-91% (see Table 3). The reactor uses an internal spring to compress the bed in a percolation reactor as hydrolysis occurs. It assures a well-behaving packed bed reactor operation with a relatively constant bulk packing density throughout the entire hydrolysis process. The kinetics of yellow poplar cellulose hydrolysis using prehydrolyzed sawdust in either a batch or a non-shrinking bed (no internal spring) percolation reactor is seen in Figure 3.

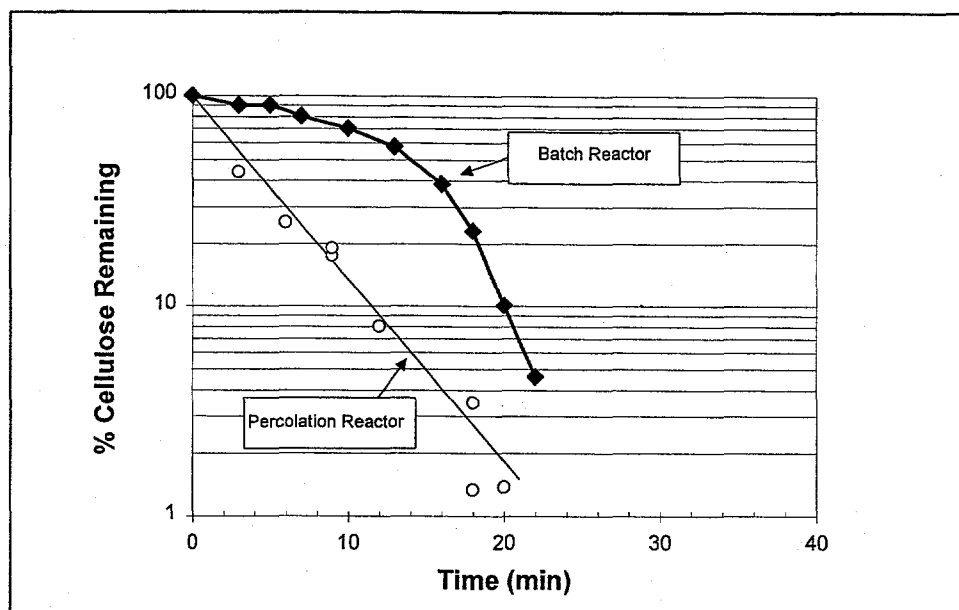


Figure 3. Hydrolysis of Prehydrolyzed Yellow Poplar at 225°C Using 0.07% Sulfuric Acid (Batch Reactor and Flow-Through Percolation Reactor)

Recognizing the importance of this finding, especially the difference in the kinetic behavior observed from the two types of reactors, these experiments have been repeated several times and the data were reconfirmed. A telling observation here is the five-fold difference in the initial rates differences between the two cases, flow-through shrinking-bed reactor and the unstirred batch reactor. Using Saeman's¹³ extrapolated hydrolysis kinetic equations and constants from Douglas fir cellulose at 225°C and 0.07% w/w sulfuric acid (Saeman's lowest acid concentration was 0.4%), an extrapolated rate constant of 0.07 min^{-1} is obtained. We find this to agree reasonably well with our batch data of 0.06 min^{-1} (a rate constant taken from the initial slope of Figure 3 (0-5 min) and multiplied by 2.303). The 5-fold higher rate observed in the flow-through percolation reactor indicates that the actual cellulose hydrolysis rate is much faster than the rate projected from the batch data. The main difference between the two reactor systems is the reaction media. In the flow-through reactor, the acid solution is relatively fresh at all time, whereas the media in the batch reactor contains more reaction products such as carbohydrate oligomer and monosaccharides, acid-soluble lignin, and decomposing and the re-condensing components of lignin and carbohydrates.

To identify how reaction media affects the cellulose hydrolysis, a series of experiments have been conducted. Figure 4 shows that different hydrolysis rate are

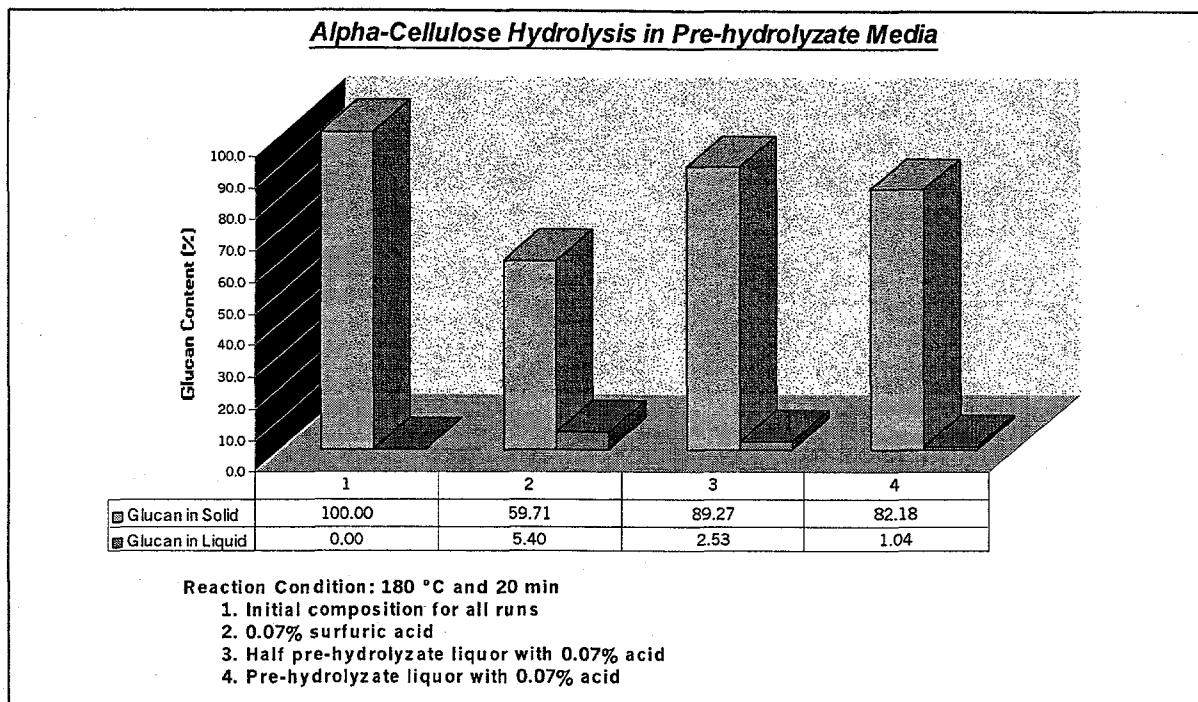


Figure 4. Comparison of α -Cellulose Hydrolysis at Different Media

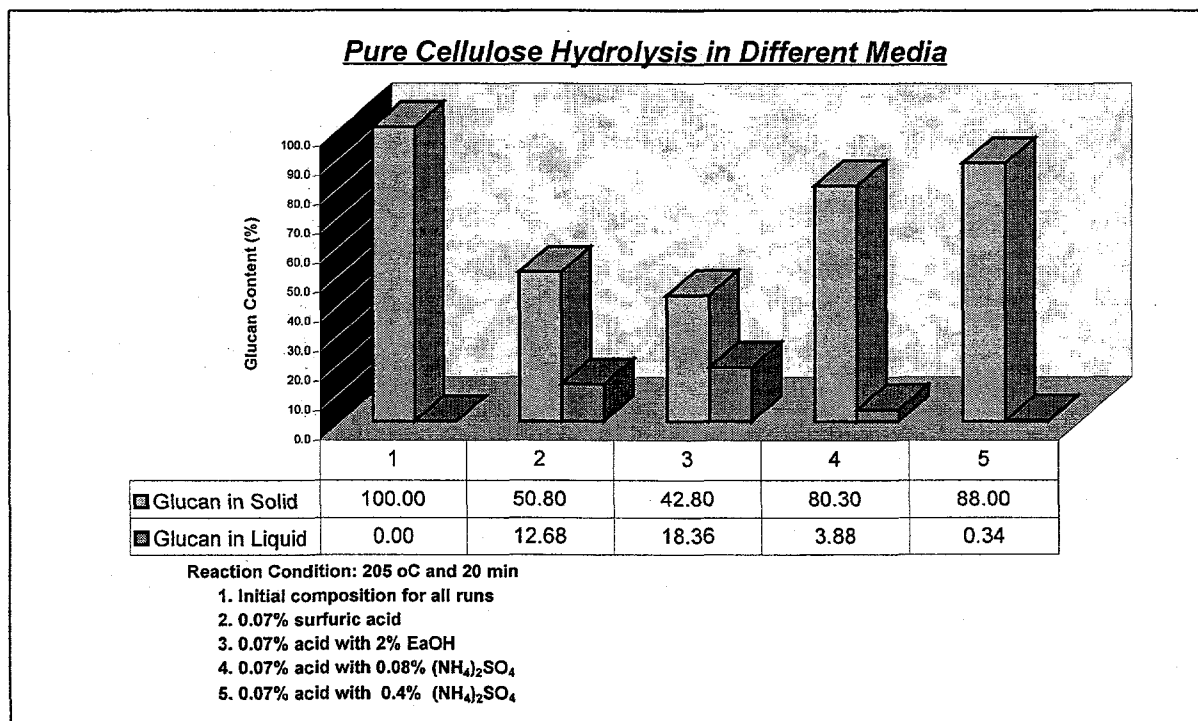


Figure 5. Pure Cellulose Hydrolysis at Different Sulfuric Acid Media by adding EtOH or $(\text{NH}_4)_2\text{SO}_4$

observed when α -cellulose reacted with different starting media. With pure sulfuric acid solution, α -cellulose hydrolyzes much faster than it would in a pre-hydrolyzed yellow poplar media. The prehydrolyzate was prepared by hot water leaching of the yellow poplar at 180 °C to remove hemicellulose and a part of the lignin. Because hemicellulose hydrolyzes at lower temperature and at faster rate than cellulose, similar reaction environment as that of the pre-hydrolyzate media is expected for cellulose hydrolysis in batch reactor. The hypothesis here is that cellulose hydrolysis could be significantly hindered by the reaction media. The results summarized in Figure 5 show that although the hydrolysis was enhanced slightly by presence of Ethyl Alcohol (EaOH), the present of certain salts such as $(\text{NH}_4)_2\text{SO}_4$ could slow down the cellulose hydrolysis dramatically. We thus postulate that cellulose hydrolysis occurring in a batch reactor can be greatly affected by the contents of hydrolyzate media of itself and by the components externally supplied. Further research is being planned to verify how individual components in the hydrolyzate liquor, including monosaccharides and their decomposed products, affect the rate of cellulose hydrolysis.

Another striking observation not foreseen from the literature information is the totally different behavior of hydrolyzate liquor between flow-through reactor and the batch reactor under extremely dilute acid (0.07%) condition. The data shown in Tables clearly indicate that the glucan yield (expressed by glucose presented in hydrolyzate liquor) is consistent at 80-90 % level for the flow-through reactors. However, the yield of glucose in batch reactors is less than 40% at the same condition. Whether this phenomena prevail under higher acid condition is unknown. We plan to run more flow-through percolation experiments at different acid levels for further identification. Because the glucose decomposes at a relatively low rate at the reaction condition, it is unlikely that the low glucose yield in batch reactors is due to decomposition. Then where has the glucose gone? We think that the answer to this question has to do with the hydrolysis media produced during the reaction. Further experiments were carried out to follow up on this issue. The experiments were designed to investigate how glucose 'decomposes' in different media. The results are shown in figures 6 & 7. These results reveal that glucose undergoes a certain pathway yet to be identified in the pre-hydrolyzate liquor and rapidly disappears. Especially at 0.07 % w/w sulfuric acid condition in the pre-hydrolyzate media, which NREL proved to be the optimal acid concentration for percolation reactions, the glucose

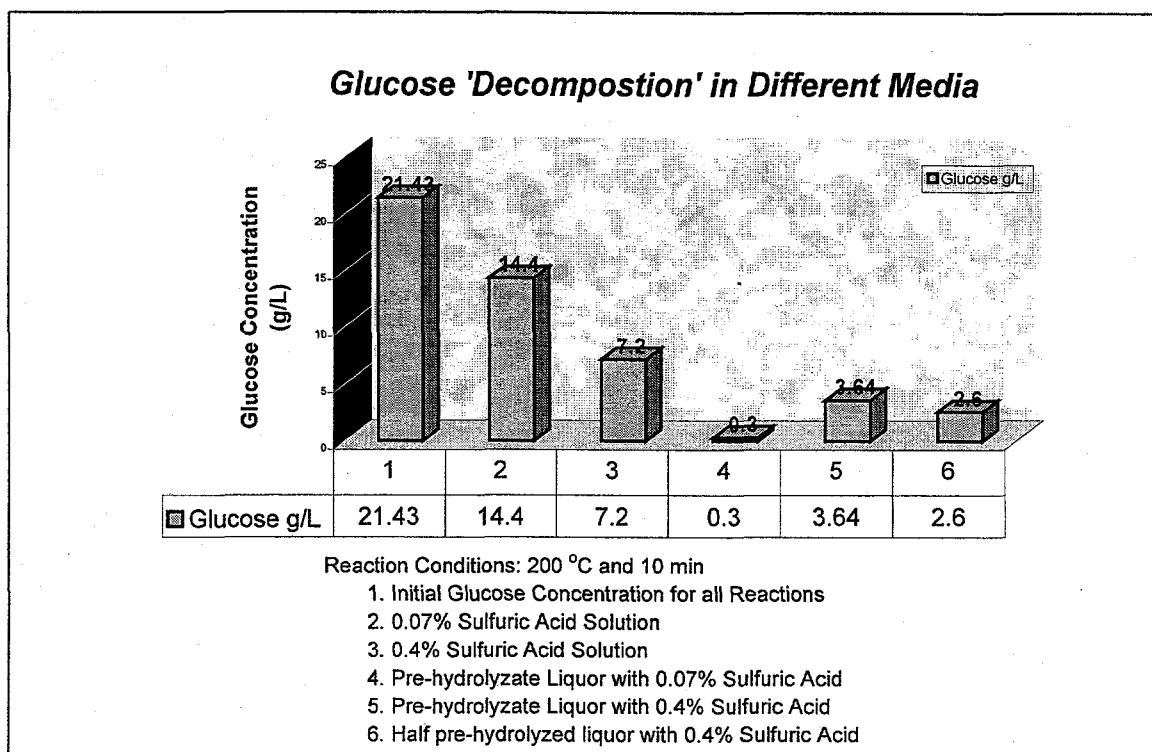


Figure 6. Comparison of Glucose 'Decomposition' Rate at Different Reaction Media - Effect of Pre-hydrolyzed Liquor and Acid Concentration

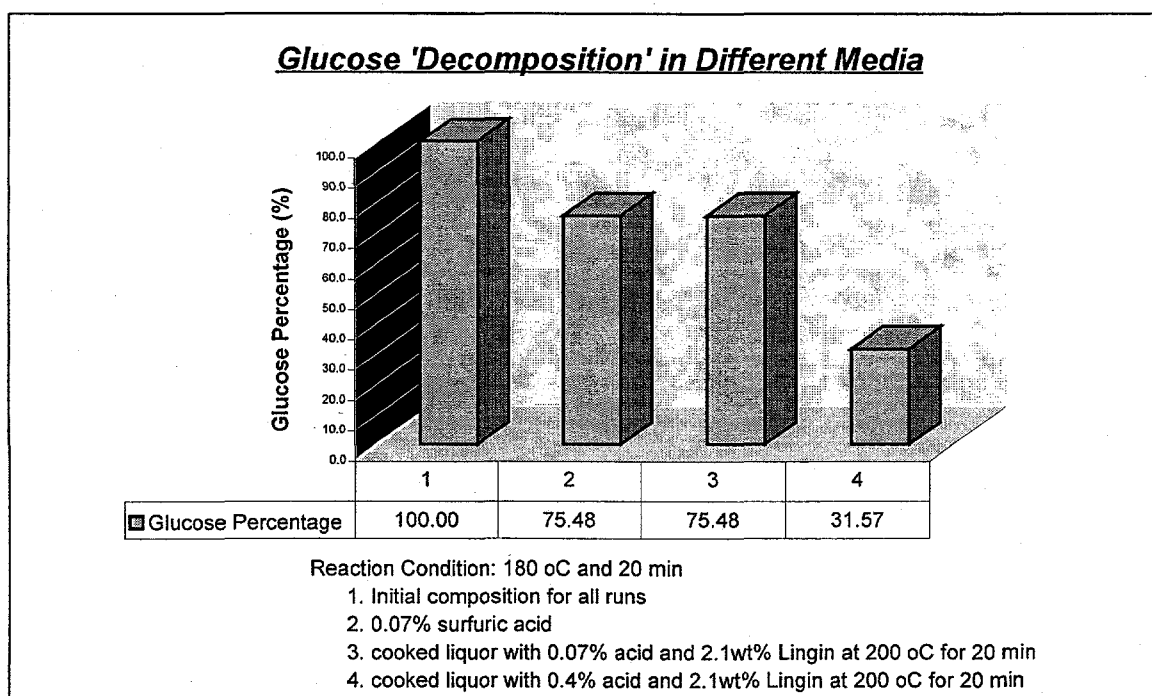


Figure 7. Comparison of Glucose 'Decomposition' Rate at Different Reaction Media - Effect of Acid Hydrolysis Reprecipitated Lignin

disappears even faster. The glucose disappearance is less with higher acid level. This certainly cannot be simply explained by glucose decomposition. There must be some unidentified reactions between glucose and some components in the hydrolyzate media. These reactions occur mainly at high temperature and are obviously affected by acid concentration (or pH) in the hydrolyzate. This is a part of the reasons why extremely high glucose yield is achieved in a shrinking-bed flow-through reactor. Further kinetic experiments are planned to further clarify this issue.

New Kinetic Model (Figure 8) Development

Based on the current experimental data, we propose a general kinetic model that includes most of the plausible reaction pathways surrounding the acid catalytic cellulose hydrolysis (see Figure 8). We have mentioned previously about the possible effects of the hydrolyzate media to the cellulose rate and glucose 'decomposition' rate. We also believe that a certain fraction of glucose exists on the surface of solid cellulose. It is attached by hydrogen bonding. If so, the breakage of glucosidic bond during hydrolysis may require extra energy to break the hydrogen bonds connected to the cellulose macrostructure. Work is currently in progress to verify this premise. Experiments are being prepared to test if cellulose hydrolysis rate can be enhanced by adding a surfactant or a polar solvent such as EtOH or Acetone by which the surface tension of the reaction media is decreased.

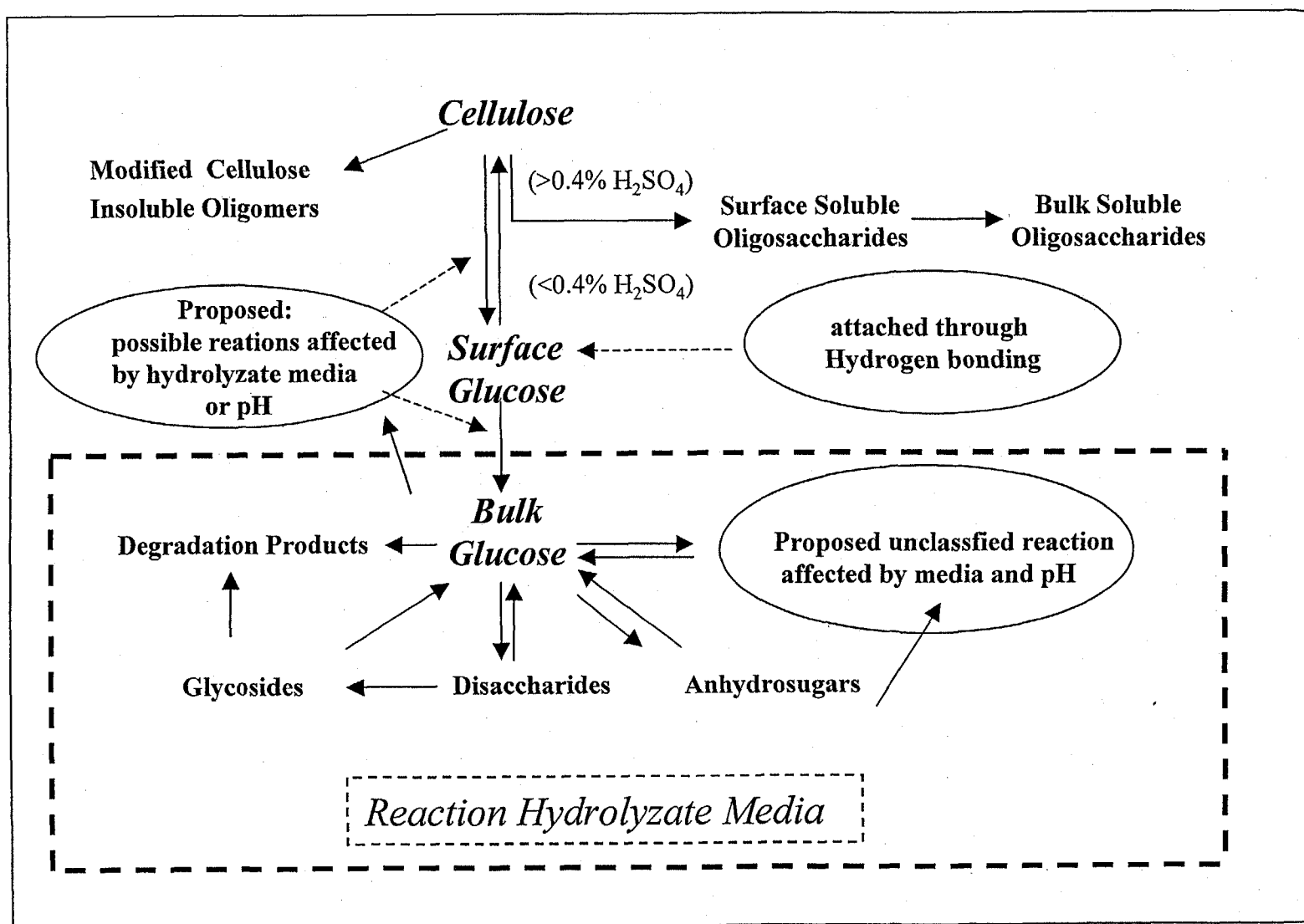


Figure 8. Proposed model for dilute acid catalyzed hydrolysis of hardwood cellulose

Table 1. % Glucose remaining after batch reaction using pretreated Yellow Poplar Feedstocks at different temperatures.

Time(min.)	205 C		220 C		235 C	
	Solid(%)	Liquid(%)	S	L	S	L
0	100	0	100	0	100	0
3	95.5	0	95.11	0	94.31	0
5	83.72	3.32	80.36	3.96	79.93	5.63
7	70.16	11.54	68.72	15.72	68.37	15.79
10	60.74	19.73	57.38	22.69	53.46	20.43
13	52.59	29.71	49.45	35.45	43.34	18.72
16	40.38	26.62	36.74	30.73	38.09	13.29
20	17.71	19.48	14.29	27.77	9.47	7.36
25	6.88	15.36	6.03	25.24	0	3.11
30	0	13.72	0	20.65	0	0

Table 2. % Glucose remaining after batch reaction using untreated Yellow Poplar Feedstocks at different temperatures.

Time(min.)	205 C		220 C		235 C	
	Solid(%)	Liquid(%)	S	L	S	L
0	100	0	100	0	100	0
3	92.23	0	90.47	3.31	89.56	3.61
5	80.21	4.11	77.29	6.75	75.53	6.88
7	67.43	15.56	61.44	20.48	60.14	21.45
10	58.64	23.35	51.46	30.12	49.52	30.33
13	48.95	35.22	43.36	40.55	40.76	45.19
16	30.12	30.23	29.45	50.98	25.56	49.82
20	14.03	27.65	11.2	45.56	6.51	47.63
25	4.67	20.26	3.14	40.25	0	42.22
30	0	20.37	0	29.97	0	33.16

Table 3. % Glucose remaining after bed-shrinking flow-through reaction using untreated Yellow Poplar Feedstocks at different temperatures.

Time(min.)	205 C		220 C		235 C	
	Solid(%)	Liquid(%)	S	L	S	L
0	100	0	100	0	100	0
3	72.08	13.13	69.75	17.25	70.25	15.87
5	65.33	24.7	58.42	30.33	50.07	36.65
7	48.72	42.56	40.39	49.55	37.72	50.91
10	33.65	55.34	29.17	66.13	20.19	67.73
13	19.44	70.49	10.05	78.85	7.34	80.14
16	9.24	80.77	3.66	89.36	2.37	90.22
20	3.17	86.65	0	90.32	0	90.78
25	0	87.54	0		0	
30	0		0			

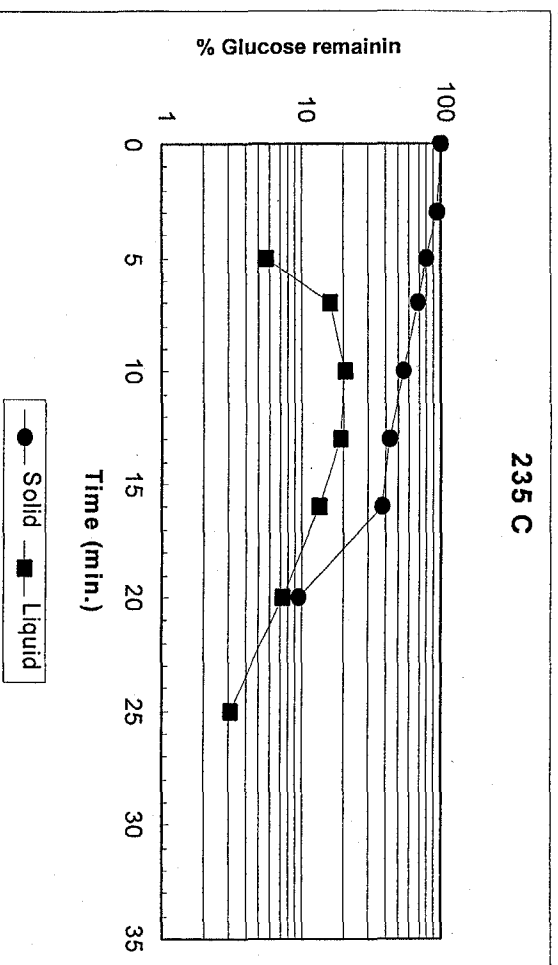
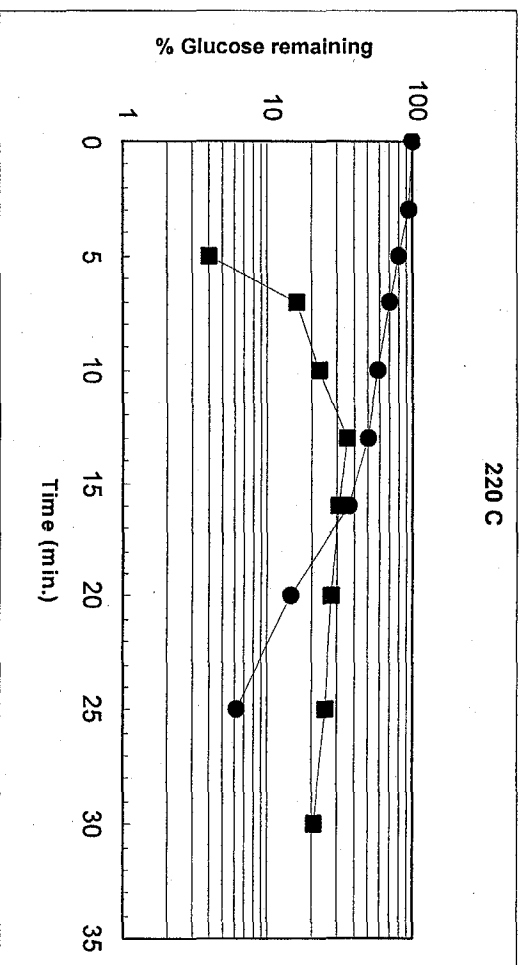
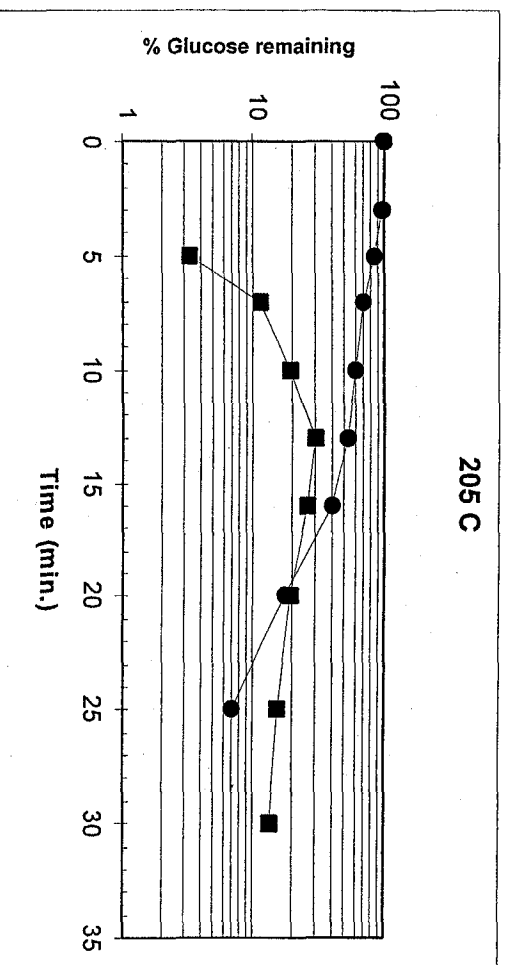


Figure 9. Semi-log plots of cellulose hydrolysis(pretreated biomass) by batch reaction as temperatures versus hydrolysis time.

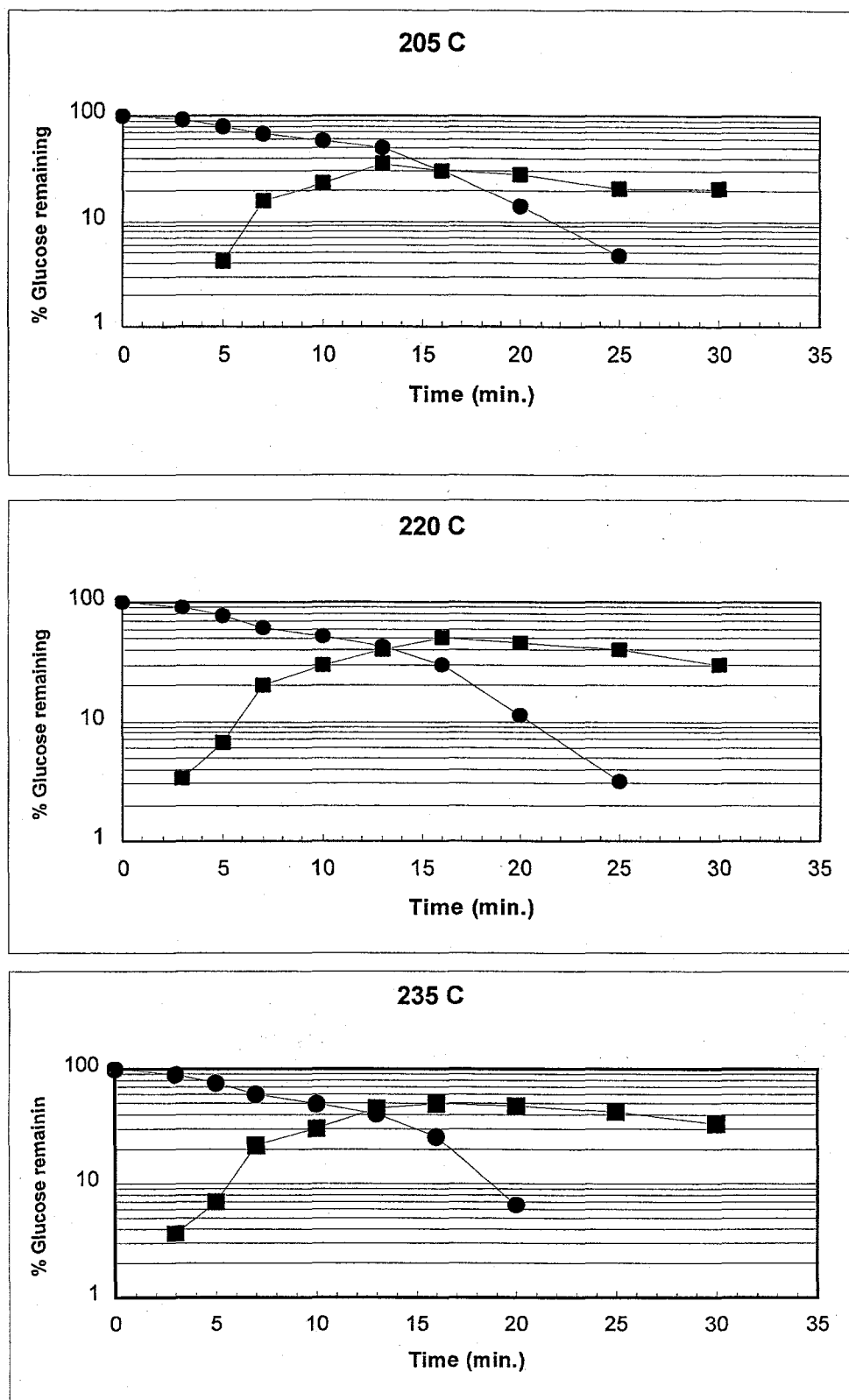


Figure 10. Semi-plots of cellulose hydrolysis (untreated biomass) by batch reaction as temperatures versus hydrolysis time.

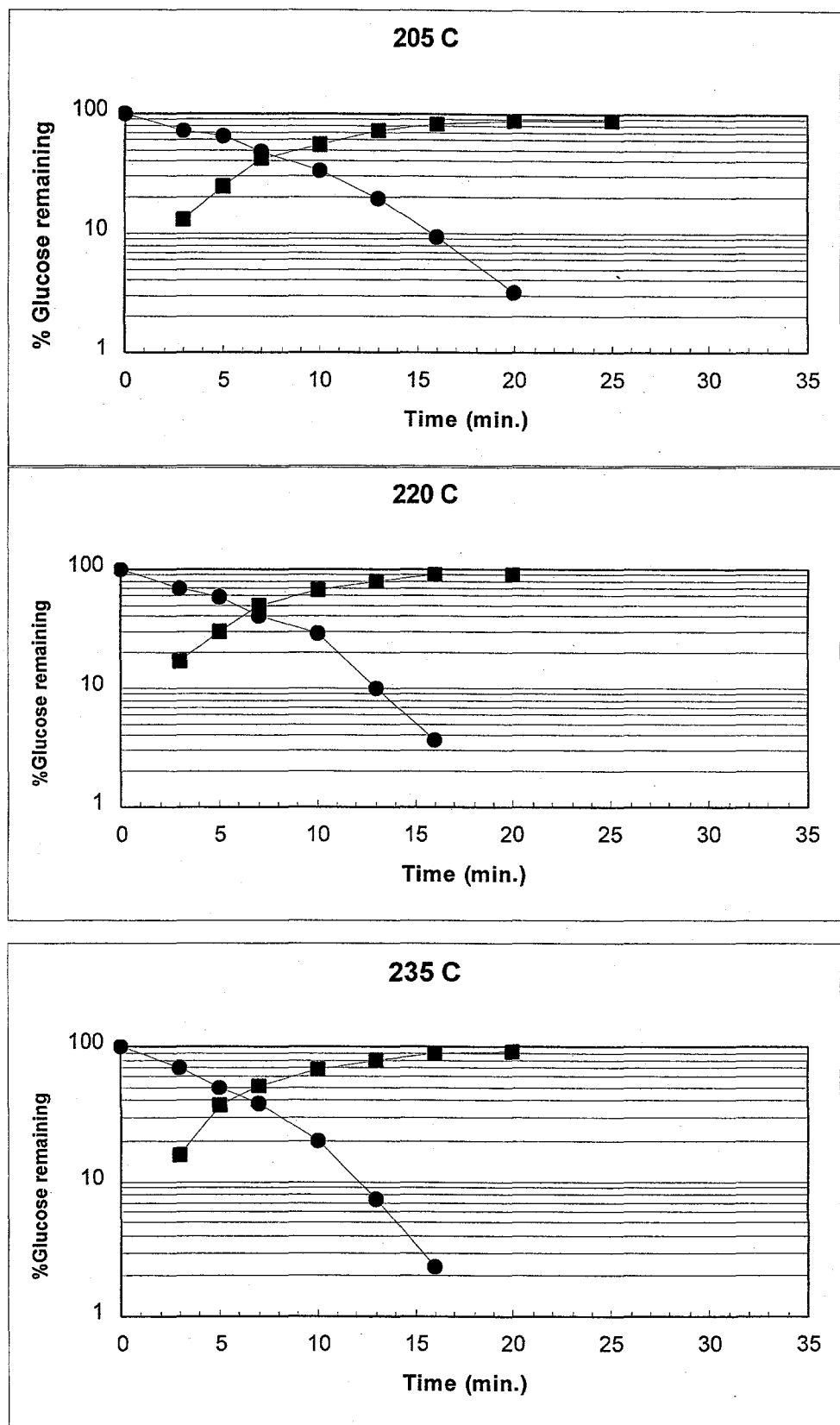


Figure 11. Semi-plots of cellulose hydrolysis (untreated biomass) by flow-through reaction as temperatures versus hydrolysis time.

References

1. Fengel, D.; Wegener, G. **Wood Chemistry, Ultrastructure, Reactions**. Walter de Gruyter: Berlin. New York, 1984, 268-274.
2. Shafizadeh, F. **Tappi**. 1963, 46, 381-383.
3. Timell, T.E. **Can. J. Chem.** 1964, 42, 1456-1472.
4. Harris, J.F. **Appl. Polym. Symp.** 1975, No.28, 131-144.
5. Philipp, B.; Jacopian, V.; Loth, F.; Hirte, W.; Schulz, G. Influence of Cellulose Physical Structure on Thermohydrolytic, Hydrolytic and Enzymatic Degradation of Cellulose. In: **Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid Catalysis**. Edit by Brown, Jr. R. D.; Jurasek, L. Adv. Chem. Ser. 181, ACS, Washington, D.C. 1979, 127-143.
6. Sjöström E. **Wood Chemistry: Fundamentals and Applications**. 2nd edition. Academic Press, Inc., San Diego, California. 1993, 44-46.
7. Popoff, T.; Theander, O. **Carbohydr. Res.** 1972, 22, 135-149.
8. Popoff, T.; Theander, O. **Acta Chem. Stand.** 1976, 30, 397-402.
9. Root, D.F.; Harris, J.F.; Saeman, J.F.; Nwill, W.K. **For. Prod. J.** 1959, 9, No.5, 158-161.
10. Vink, H. **Makromol. Chem.** 1966, 94, 1-14.
11. Millett, M.A.; Baker, A.J.; Satter, L. D. **Biotechnology and Bioengineering Symposium No. 6**. John Wiley: New York, 1976, 125-153.
12. Cowling, E.B.; Kirk, T.K. **Biotechnology and Bioengineering Symposium No. 6**. John Wiley: New York, 1976, 95-123.
13. Saeman, J. F. (1945), **Ind. Eng. Chem.** 37, 42-52.
14. Springer, E. L. **Tappi**. 1966, 49, 102-106.
15. Daruwalla, E. H.; Shet, R. T. **Text. Res. J.** 1962, 32, 942-954.
16. Nelson, M. L. J. **Polym. Sci.** 1960, 43, 351-371.
17. Millett, M. A.; Effland, M. J.; Caulfield, D.F. Influence of Fine Grinding on the Hydrolysis of Cellulosic Materials - Acid vs. Enzymatic. In: **Hydrolysis of**

Cellulose: Mechanisms of Enzymatic and Acid Catalysis (Brown, Jr. R. D. and Jurasek, L., Eds.). Adv. Chem. Ser. 181, ACS, Washington, D. C., 1979, 71-89.

18. Conner, A. H., Wood, B. F., Hill, C. G., Harris, J. F. In: **Cellulose: Structure, Modification and Hydrolysis** (Young, R. A. and Rowell, R. M., eds.). J. Wiley and Sons, New York, NY. 1986, 281-296.
19. Conner, A.H.; Wood, B.F.; Hill, C.G.; Harris, J.F. Kinetic Model for the Dilute Sulfuric Acid Saccharification of Lignocellulose. **J. Wood Chem. Technol.** 1985, 5, 461-489.
20. Bouchard, J.; Abatzoglou, N.; Chornet, E.; Overend, R.P. **Characterization of Depolymerized Cellulosic Residues**. Springer-Verlag 1989, 343-355.
21. Mok, W.S.; Antal, M.J. Productive and Parasitic Pathways in Dilute Acid-Catalyzed Hydrolysis of Cellulose. **Ind. Eng. Chem. Res.** 1992, 31, 94-100.
22. Torget, R.W.; Hayward, T.K.; Elander, R. Total Hydrolysis of Lignocellulosic Biomass using Very Dilute Acid Employing a Novel Shrinking Bed Reactor Configuration. **19th Symposium on Biotechnology for Fuels and Chemicals**. 1997, Colorado Springs, CO.