Quarterly Progress Report
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(For the period of **April 1- June 30, 2000**)

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

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SYNOPSIS

The primary emphasis of the project work during this period was again placed on the Task I. The experimental kinetic investigations were continued using batch reactors (the experimental set-up previously reported) and the bed-shrinking flow-through (BSFT) reactors. From the experimental findings accumulated to this point, we have confirmed that the earlier research work of NREL that the BSFT 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, 230 °C. We have acquired data that further support that the yields far above "the theoretical glucose yield of 70%[1]" are achievable. This indeed represents a breakthrough and a milestone event in the acid hydrolysis technology dilute-acid hydrolysis technologies. We are in the process of laying the foundation of the kinetics of dilute-acid hydrolysis of cellulosic biomass. Our goal is to gain fundamental understanding of the reactions and other rate processes involved in this complex process. The recent progress on the work along theses lines is summarized in this report.

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

A. Review of Previous Acid Hydrolysis Study and Bed-Shrinking Flow-Though (BSFT) Reactor

Previous researchers have frequently employed batch reactors in kinetic investigations of acid hydrolysis of cellulose. The first kinetic model was suggested by Saeman[2] as a simple chain reaction: cellulose → glucose → degradation products. A sample of projected profile of glucose based on the classical kinetic parameter of Saeman is shown in Figure 1. This is in agreement with the kinetic finding that the activation energy of hydrolysis reaction is higher that of decomposition. The maximum yield in a batch reactor shown in Figure 1 is only about 40% at 210°C. Application of higher temperature, although it would increase the yield in theory, is simply not feasible because of operational difficulties originating from rapid reaction rate. There have been several improvements to the original kinetic model. However, these models substantiate the results predicted by Saeman that glucose yields higher that 60-65% are not attainable. Conner et al.[3] suggested that once glucose is formed under reaction conditions, it can derivatize and/or degrade via oxidation reactions or polymerization reactions. Bouchard et al.[4] 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 substrate is not quantified as cellulose and can no longer be hydrolyzed to release glucose. Mok and Antal[5] 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.
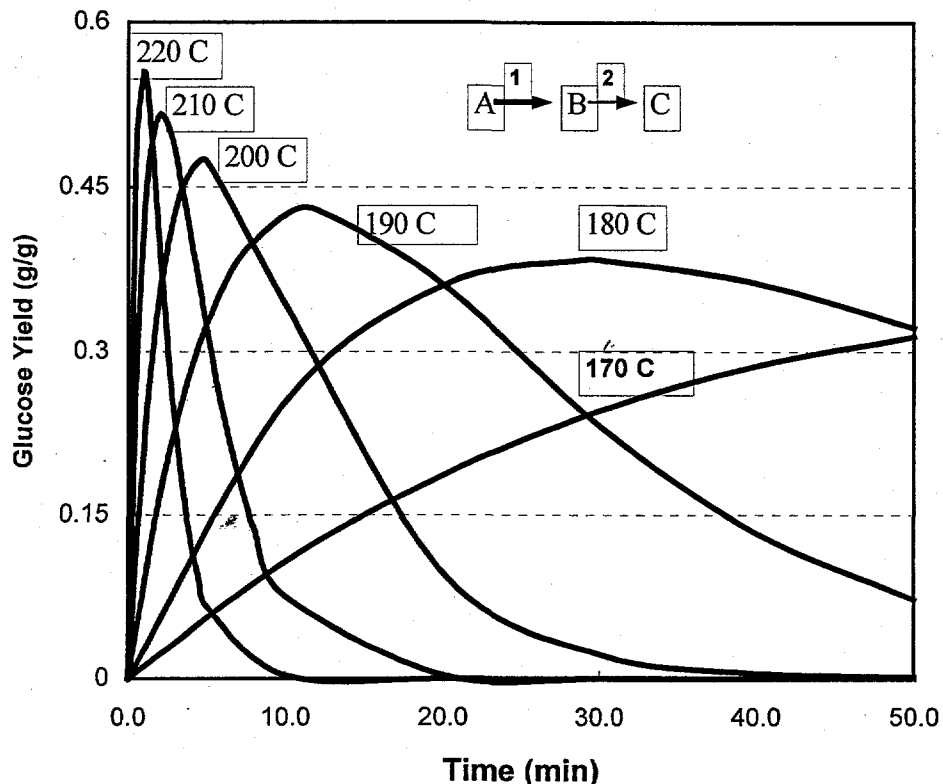
Figure 1. Glucose yield as a function of time. Yield is calculated using the rate constants of Saeman(1945), 1 wt% sulfuric acid.

In studying 'dilute' sulfuric acid fractionation catalysis of lignocellulosics, acid concentrations of 0.4 wt% to 1-2 wt%[2,3,6] are commonly used. These conditions require that exotic alloys for corrosion resistance be used to construct the hydrolysis reactors. Also, the higher the acid concentration, the more gypsum is produced due to lime input for neutralization. This creates fouling concerns in downstream processing in addition to increased disposal costs. It was a recent development that acid concentrations as low as 0.07 wt% were applied. The extremely low-acid conditions allow for lower-cost alloys for construction of industrial-scale reactors. It might also reduce the amount of gypsum. Additionally, Zucher-Hammet plots of cellobiose hydrolysis[7] and glucose degradation[8] suggested that an acid concentration equivalent to pH (measured at ambient conditions) of 2.2, which translates into an acid concentration of 0.07 wt%, would favor higher glucose yields.

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These observations on the reaction kinetics are based on conventional batch-type reactors. The rate of glucose decomposition during cellulose hydrolysis is proven to be rapid under the extremely low-acid and high temperature conditions. With realization that high yield of glucose is impossible with batch-typed reactors, researchers over the years have tested various kinds of reactors including Plug Flow Reactor (PFR), Percolation Reactors, and most notably the Bed-Shrinking Flow-though (BSFT) Reactor. The continuous version of the BSFT has also been developed at NREL. It has the flexibility of co-current or counter-current operation. We have recently published a comprehensive review article on the progress of reactor technology in acid hydrolysis[9].

The percolation reactor is a packed-bed flow-through reactor. It has certain advantages over a straight batch reactor or a PFR. First, the sugar product is removed as it is formed. This provides some important benefits that it reduces sugar decomposition and hydrolyzate detoxification later on, thus we believe this is the main reason for the extremely high glucose yields we got. Second, a packed-bed reactor can be operated with a high solid-to-liquid ration thus a relatively high concentration of the sugar can be obtained. Third, unless the feedstock is in extremely fine particles, the liquid product is separated as it leaves the reactor so the solid/liquid separation is not necessary as it as it would be in a batch reactor or a PFR.

ed-Shringking Flow-Through Reaction (BSFT)

Substrate : Yellow Poplar
        45.23% Glucan, 15.75% Xylan, 18.44% K.Lignin

1. Internal Reactor Volume : 294.4 cm3

2. Initial Working Volume : 107.3 cm3

3. Initial Biomass Weight : 65.0 g
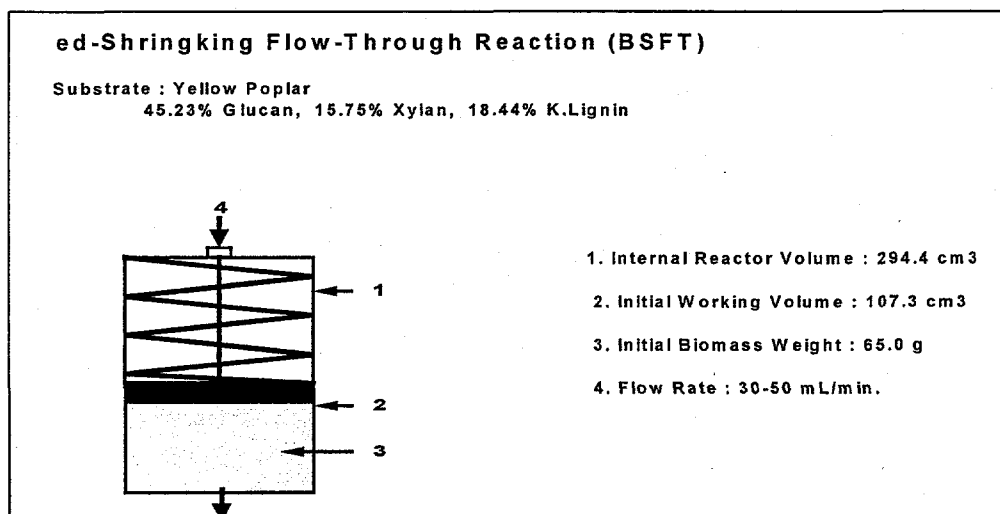
4. Flow Rate : 30-50 mL/min.

Figure 2. The Shrinking-Bed Reactor used in our lab

Torget et al. (1997) of NREL invented the Bed-Shrinking Flow-Though (BSFT) reactor. It is designed to take full advantage of the effect of bed-shrinking during the acid hydrolysis

process. To this point, it has been studied as a proof-of-concept type reactor designed specifically to keep the bed packing density constant. Because of consistent liquid flow pattern and a relatively low bed voidage in the reactor, the liquid in the BSFT reactor has a shorter resident time in comparison to percolation reactors. Less sugar decomposition is expected. High yield is therefore achieved without decreasing the product concentration. Figure 2 gives the schematics of the BSFT reactor used in our experiments.

B. Further Experimental Kinetic Study using BSFT Reactors

The cellulose hydrolysis using the bed-shrinking flow-through (BSFT) reactor was conducted for Task I-2. The initial series of experiments were done with yellow poplar using batch and BSFT reactors at the reaction temperatures of 205, 220, and 235 °C (previously reported). During this project period, the BSFT kinetic experiment was conducted with 0.07 wt.% H_2SO_4, and at reaction temperature of 180 °C. The results are summarized in Table 1 and Figure 3.

Table 1. Data of acid hydrolysis using bed-shrinking flow-through reaction for Yellow Poplar feedstock at 180 °C

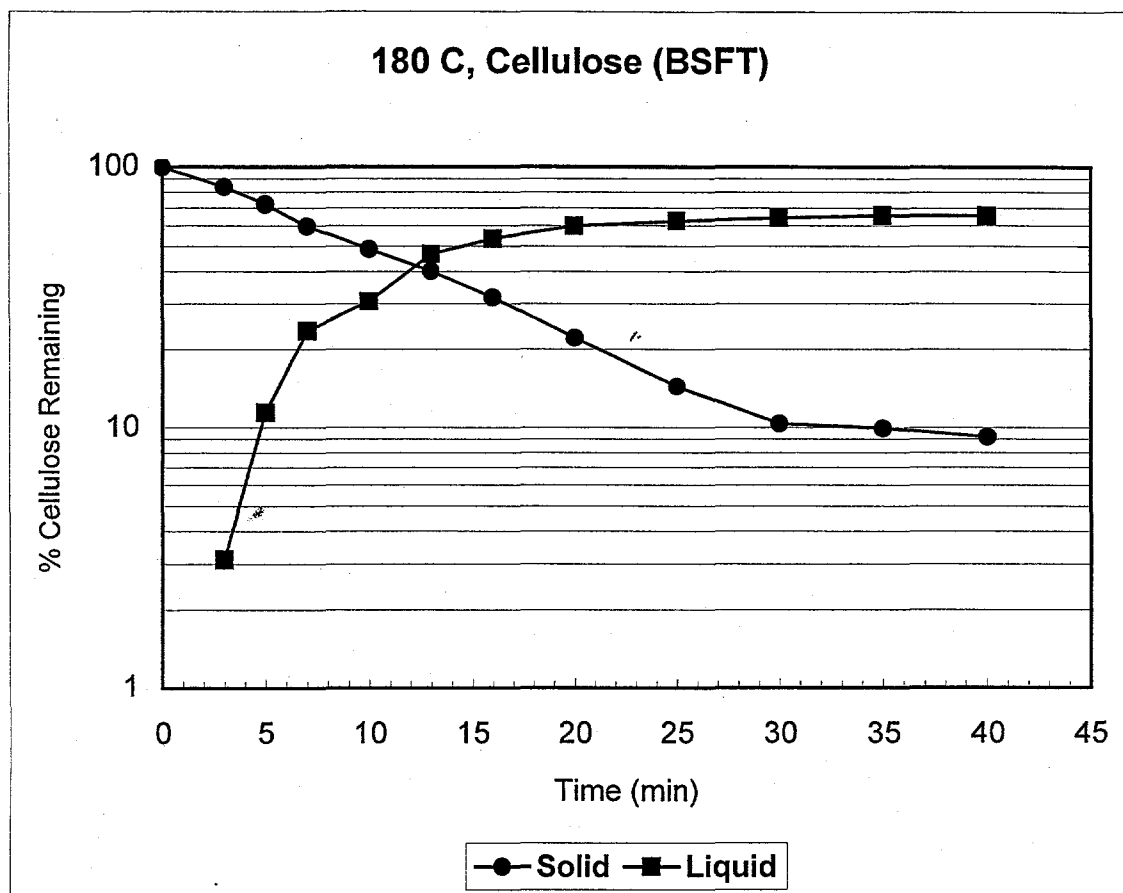| Time (min) | Cellulose | | |
| | Solid(glucan) | Liquid(glucose) | |
	Yield (%)	Yield (%)	Concentration(g/L)
0	100	0	0
3	83.95	3.12	6.1
5	72.25	11.43	13.4
7	59.63	23.64	19.9
10	48.72	30.59	18
13	40.09	46.57	21.1
16	31.65	53.36	19.6
20	22.17	59.88	17.6
25	14.45	62.43	14.7
30	10.36	64.21	12.8
35	9.93	65.66	11
40	9.2	65.54	9.6

Figure 3. Semi-log plots of cellulose hydrolysis (yellow poplar) using bed- shrinking flow-through reaction at 180 °C .

The major findings in this experiment are as follows:

1. The maximum yield of glucose from yellow poplar using bed-shrinking flow-through reactor is about 65% for 180 °C. This is much higher than that using batch reaction condition (12.76% at 180 °C, previously reported). But, this yield (65%) is much lower than those of earlier work at 205 - 235 °C (87.54 – 90.78%).

2. The maximum concentration of glucose in the collected liquor is 21.1 g/L, which occurs at the reaction time of 13 min.

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Follow up experiments are currently being conducted the biomass hydrolysis using BSFT reaction at 195 °C. Upon completion of this work, we should be able to verify the profile of cellulose hydrolysis using BSFT reactor over the reaction temperatures of 180 - 235 °C. Further kinetic experiments are planned to refine the optimal reaction condition of biomass hydrolysis specifically for a BSFT reaction process. Variations of reaction temperature and flow rate are being considered as a means to improve the reactor performance.

C. Experimental Study on Glucose Decomposition

A significant improvement on glucose yield is achieved with use of BSFT reactors over batch reactors under extremely dilute-acid conditions. Among the various factors affecting the glucose yield, glucose decomposition is believed to play a major role in it. The glucose formed during hydrolysis is removed immediately in the BSFT reactor whereas in a batch reactor it must face the reactor condition throughout the entire hydrolysis process. Literature information on glucose decomposition is rather scarce especially at extremely dilute acid concentration, the region of our interest. do hydrolysis. Although kinetics parameters can

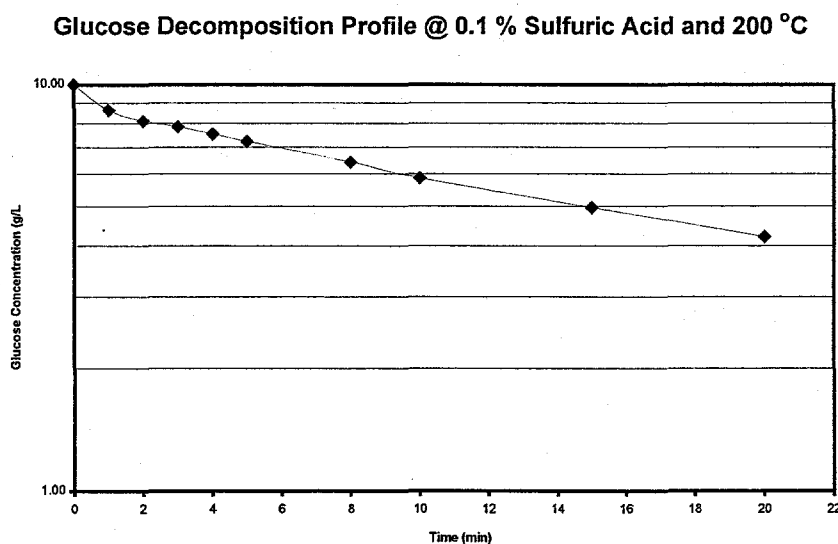**Glucose Decomposition Profile @ 0.1 % Sulfuric Acid and 200 °C**

Figure 4. Glucose Decomposition Profile vs. Time

be extrapolated to low acid region from literature data, we feel it is necessary to conduct glucose decomposition study at the conditions of our BSFT reaction. The experiments were

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thus conducted using stainless steel bomb reactors. Fluidized sand-baths were used for temperature control. Figure 4 shows the decomposition profile of glucose at 200 °C, and 0.1% acid medium. Additional experimental data covering broader range acid concentration are shown in Table 2 and Figure 5.

Table 2. Effects of Acid Concentration on Glucose Decomposition
      @ 200 °C with initial 20 g/L of Glucose

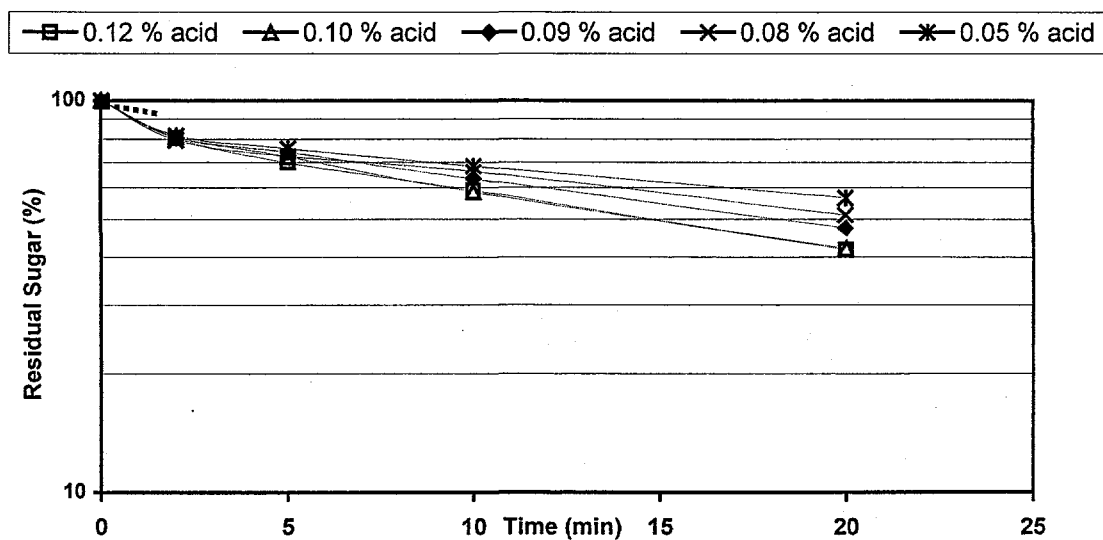| Time | Glucose Residual (%) | | | | |
| | Sulfuric Acid Concentration | | | | |
(min)	0.12% Acid	0.10% Acid	0.09% Acid	0.08% Acid	0.05% Acid
0	100	100	100	100	100
2	80.43	81.2	80.56	79.48	81.68
5	69.7	72.34	74.21	72.38	75.85
10	59.03	58.55	63.23	66.11	68.37
20	41.72	41.95	47.43	51.21	56.52

Figure 5. Profile of Glucose Decomposition at Different Acid Medium

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D. Experimental Results Discussion

The straight lines shown in the semi-log plots of Figure 4-5 indicate that at the temperature and acid concentration tested, the decomposition of glucose follows first order reaction mechanism. In this respect, our data are quite similar to the kinetic data of Saeman[2] (Figure 6). It is noteworthy that all the decomposition data (including Saeman's) have a common feature which has been overlooked in the kinetic model. All the straight lines do not back track to original glucose concentration at time zero (which is 100 % glucose residual) on glucose degradation semi-log plot. Actually these lines when extrapolated to time zero, they adjoin at 80-90 % glucose residual. What then happened to the 10-20 percent of total glucose at the beginning? We think it is an indication that there are reversible reaction pathways and that the reversible reaction are much faster the irreversible glucose decomposition reaction. The reversible reactions can therefore attain equilibrium at the early phase of the reaction. The prove is found in previous studies on reaction pathway for glucose decomposition in aqueous solution.
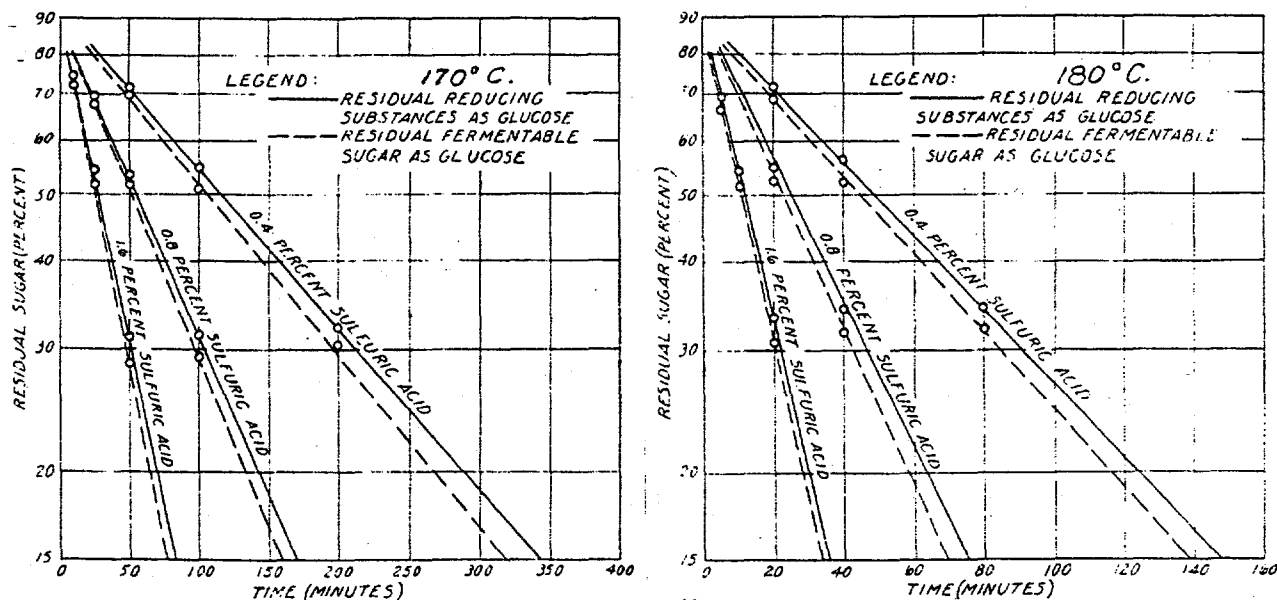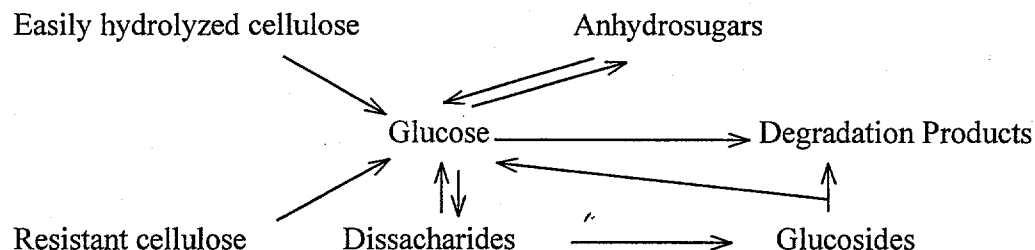

Figure 6. Glucose Decomposition Semi-log Plot from Saeman's Work[2]

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An extended kinetic model was suggested by Conner et al. which incorporates the reversion reactions of glucose[3]:

Easily hydrolyzed cellulose   Anhydrosugars

Glucose ⟶ Degradation Products

Resistant cellulose   Dissacharides ⟶ Glucosides

They have also developed a complicated mathematic model for cellulose saccharification including the glucose decomposition, reverse reaction and disaccharide dehydration. With implementation of the modified kinetic model, such as inclusion of the reversion reactions, the fit of experimental data to the predicted model has been greatly improved. However, the model for glucose decomposition did not fit well with experimental data. A number of researchers who have conducted mechanistic studies of glucose reactions in aqueous solutions found that the isomerization of glucose to fructose (and mannose) was found to be an important reaction pathway, especially under mild acid conditions[11]. The fructose itself is also subjected to decomposition and other reversible reactions after formed from glucose though the reversible isomerization reactions. If we add this reversible isomerization reaction pathway to above kinetic model plus the decomposition of fructose pathway, a more complicated kinetic model is expected.
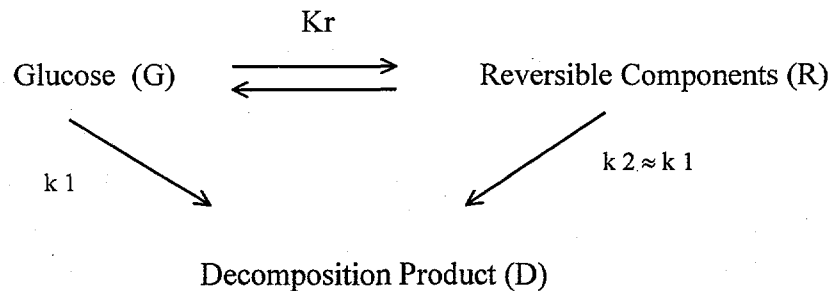
Assuming that glucose decomposition reaction (exclude all reversible reactions) follow the first order mechanism, certain conclusions can be drawn out of the glucose residual profiles of our experimental data. First, these reversible reactions, including isomerization and dehydration, have a much greater reaction rate that glucose decomposition and equilibrium is reached within the early phase of the reaction. Second, straight lines are obtained once the equilibriums are established. It indicates that the components produced from reversible reaction are also subjected to decomposition and it occurs at approximately the same rate as glucose decomposition. Otherwise, the straight lines cannot be obtained. Third, acid concentration and temperature will affect both the glucose decomposition rate and the

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reversible reactions rate. Based on these conclusions, we propose a simplified mathematics model for the glucose decomposition mechanism.

E. A Simplified Kinetic Model for Glucose Decomposition

For development of this model, the following assumptions are applied.

(1). There may be more than one reversible reaction. If so, they are lumped into one reversible reaction and we use Kr for the equilibrium constant.

(2). The total reversible reaction occurs instantaneously so that the reversible reaction is always at equilibrium.

(3). The glucose decomposition follows the first order and we use k_1 for the rate constant. The reversible products from glucose will decompose as well and the decomposition rate constant (k_2) is approximately equal to k_1. This assumption will give the straight lines of glucose profile in semi-log plot.

$$\text{Glucose (G)} \underset{}{\overset{Kr}{\rightleftharpoons}} \text{Reversible Components (R)}$$

k_1 $k_2 \approx k_1$

Decomposition Product (D)

(4). k_1 and Kr are both function of acid concentration and temperature and they are expressed as:

$$k1 = a^m * k_0 * \exp(-E1/RT)$$
$$Kr = a^n * Kr_0 * \exp(-\Delta H/RT)$$

'a' is [H^+] concentration (unit M) and T is temperature in K.

With these assumptions, the mass balance equations in a batch reactors are derived as follows:

$$\frac{d(G+RC)}{dt} = -k1 * G - k2 * RC$$
$$RC = Kr * G$$

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Since $k1 \approx k2$, we have:

$$\frac{dG}{dt} = -k1 * G$$

with initial condition of: at time t = 0, G + RC = G (1 + Kr) = G_0

The final glucose residual profile is obtained as:

$$\frac{G}{G_0} = \frac{\exp(-k1 * t)}{(1 + Kr)}$$

For experimental verification, a SAS regression program was generated (see Appendix) to use do determine k1 (k_0 and m value) and Kr (Kr_0 and n value)at 200 °C. The results are as follows:

$k_0 * \exp(-E_1/RT)$ = 0.6451

m = 0.7654

$Kr_0 * \exp(-\Delta H/RT)$ = 0.0866

n = -0.1743

From above data, we calculated the percentage of initial glucose that has been transformed into other form through reversible reactions. The results are summarized in Table 3.

Table 3. Percentage of Glucose Loss due to reversible reaction, @ 200 °C

Sulfuric Acid Concentration	wt %	0.05	0.07	0.10	0.15	0.40
[H+] Concentration	mol / L	0.0102	0.0143	0.0204	0.0306	0.0816
Initial Glucose Loss via Reversible Reaction	%	16.15	15.37	14.58	13.72	11.82

The above table reveals a very interesting fact that a large percent of glucose has been lost at the beginning of decomposition due to the reversible reactions. The lower acid concentration,

the larger percentage of initial glucose is transformed. At 200°C and 0.07 wt% of sulfuric acid, the theoretical maximum yield of glucose would be only about 85% instead of 100% if no method is taken to bring the reversible components back into glucose form. In most model used for biomass hydrolysis, it is commonly assumed that cellulose hydrolysis produces only monomeric glucose and that all oligosacharides in solution result from the reversion reactions. This assumption fits very well with our BSFT reactor experiments at high temperature (225°C). But if we lower the temperature in BSFT reaction to 200°C and still maintain 0.07 wt% of sulfuric acid solution, it is unlikely that we surpass the 85% of glucose yield unless we somehow mimic the effect of the reversible reaction.

Along these lines, we are currently exploring the following points:

1) Can external chemicals influence the hydrolysis and decomposition reaction? (Ethanol would be a candidate.)

2) Can one bring back the glucose (from polymerized/isomerized form) by secondary treatment of the hydrolyzate?

3) If the reversion products are identified, can one use liquor which contains those components to suppress reversible pathway? This can be done by recycling the glucose-less liquor after the hydrolyzates are fermented to ethanol.

Additional experimental work is currently in progress to further investigate the fundamental aspects of the glucose decomposition reaction.

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Appendix I.

<u>SAS Regression Program for Glucose Decomposition</u>

title 'Modeling Result of Glucose Decomposition at 200 °C';

data Gdecom;
input aa t G;
cards;
```
0.02449  2.0    0.8043
0.02449  5.0    0.697
0.02449  10.0   0.5903
0.02449  20.0   0.4172

0.02041  2.0    0.8120
0.02041  5.0    0.7234
0.02041  10.0   0.5855
0.02041  20.0   0.4195

0.01837  2.0    0.8056
0.01837  5.0    0.7421
0.01837  10.0   0.6323
0.01837  20.0   0.4743

0.01633  2.0    0.7948
0.01633  5.0    0.7238
0.01633  10.0   0.6600
0.01633  20.0   0.5101

0.0102   2.0    0.8168
0.0102   5.0    0.7585
0.0102   10.0   0.6837
0.0102   20.0   0.5652
run;
```

proc nlin data = Gdecom converge = 0.000001;
parm m=1.045 n=-0.176 A=0.45 B=0.070;
model G = exp(-A*t*(aa**m))/(1.0+B*(aa**n));

der.m = exp(-A*t*(aa**m))*(-A)*t*log(aa)*(aa**m)/(1.0+B*(aa**n));

der.n = -B*(aa**n)*log(aa)*exp(-A*t*(aa**m))/((1.0+B*(aa**n))**2);

der.A = exp(-A*t*(aa**m))*(-t)*(aa**m)/(1.0+B*(aa**n));

der.B = -(aa**n)*exp(-A*t*(aa**m))/((1.0+B*(aa**n))**2);

 run;

Appendix II.

SAS Regression Program Results for Glucose Decompositions

Modeling Result of Glucose Decomposition at 200 oC   19:02 Sunday, July 23, 2000

Non-Linear Least Squares Iterative Phase   Dependent Variable G
Method: Gauss-Newton

Iter	M	N	A	B	Sum of Squares
0	1.045000	-0.176000	0.450000	0.070000	0.684443
1	0.723524	-0.145659	0.158270	0.084908	0.533258
2	0.540278	-0.039773	0.340635	0.142966	0.048332
3	0.717446	-0.180090	0.497553	0.070362	0.018805
4	0.763155	-0.168180	0.621704	0.087778	0.004178
5	0.765066	-0.173798	0.643844	0.086839	0.003490
6	0.765366	-0.174324	0.645064	0.086621	0.003490
7	0.765382	-0.174349	0.645109	0.086612	0.003490

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics   Dependent Variable G

Source	DF	Sum of Squares	Mean Square
Regression	4	9.0584137713	2.2646034428
Residual	16	0.0034899687	0.0002181230
Uncorrected Total	20	9.0619037400	
(Corrected Total)	19	0.3282422920	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval Lower	Upper
M	0.7653823270	0.11066472838	0.53078474872	0.9999799053
N	-.1743485974	0.16119088748	-.51605631577	0.1673591211
A	0.6451087022	0.28499017855	0.04095951488	1.2492578896
B	0.0866124892	0.05748441631	-.03524842393	0.2084734024

Asymptotic Correlation Matrix

Corr	M	N	A	B
M	1	-0.738869599	0.9978203797	-0.723819083
N	-0.738869599	1	-0.747735681	0.9970258303
A	0.9978203797	-0.747735681	1	-0.736507511
B	-0.723819083	0.9970258303	-0.736507511	1