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Dilute Sulfuric Acid Hydrolysis of Biomass for Ethanol Production

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ABSTRACT

A series of pilot plant experiments have been conducted to compare the performance of a system utilizing two percolation reactors in series to a single reactor system. Although theoretically capable of producing higher glucose yields or concentrations, the two-reactor system concentrations were approximately the same and the yields were considerably lower than those from the single reactor study. An associated kinetics study found the glucose degradation kinetics to be accelerated by chromium ions, but this effect was greatly reduced in the presence of wood. The presence of metal surfaces also increased the rate of degradation even without large ion concentrations. The poor performance of the reactor system is proposed to be caused by intraparticle glucose diffusion effects and the catalytic effect on glucose degradation reactions of chromium ions from the corrosion of stainless steel by the acid. Strategies for reducing the effects of these phenomena on PBR performance are presented.

Index Entries: Acid hydrolysis; aspen; percolation; kinetics; chromium.

INTRODUCTION

Lignocellulosic biomass can be hydrolyzed using dilute sulfuric acid to produce fermentable sugars by several different process configurations. One such configuration involves the use of high temperature (180–190°C) acid hydrolysis in a series of semibatch reactors—referred to

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as a Progressing Batch Reacter (PBR) process. The PBR concept is based on the Shanks leaching process (*1*) and has been described previously (*2,3*).

During this past year, experiments have been conducted using two reactors in series. Previous to this, single reactor experiments were done to obtain baseline information for the multireactor studies to follow (*2*). For the single reactor experiments, yields of glucose ranged from 41 to 61%, and glucose concentrations from 5.9 to 11.5 g/L. Since process economics will ultimately depend on both yield and concentration, a figure of merit, Mg, was calculated as the product of the yield in % and the concentration in g/L. Figures of merit from 258 to 580 were obtained during the single reactor study. Generally, the best performance was obtained using a 185°C hydrolysis temperature, a 30-min nominal liquid residence time (empty reactor basis), and a 0.5 wt% sulfuric acid concentration.

The tandem reactor experiments were done to provide a preliminary assessment of the performance of a multireactor system relative to that of a single reactor. In parallel with this, an investigation was conducted on the kinetics of the dilute acid hydrolysis of the aspen wood used in the pilot plant experiments. The kinetics were studied to see if the glucose generation and degradation reaction kinetics proposed by J. F. Saeman applied to the wood and the conditions being used in the two-reactor pilot plant.

MATERIALS AND METHODS

Materials

The wood used for all experiments was aspen (*Populus tremuloides*), which has been debarked, air dried to 5% moisture, and chipped with a hogger. The wood contained approximately 0.492 gs of glucose potential/g of bone-dry wood. For the tandem reactor experiments, two size distributions of chips were produced using a knife mill outfitted with either a 1.27 cm round-hole screen or a 0.635 cm round-hole screen. Minus 60 mesh aspen dust was used for the kinetics experiments.

Tandem Reactor System

The two reactors that comprise the core of the tandem reactor apparatus were each constructed of a 15 cm (6 in) diameter, 0.9 m (3 ft)-long Carpenter 20 Cb-3 (CA20) pipe with carbon steel lap joint and blind flanges. The flanges are shielded from the hot acid by full face teflon gaskets. Each has a total volume of 0.017 m^3 (0.6 ft^3), and includes a steam jacket for external heating. Inserts for acid distribution and wood chip bed support are also made of CA20, as are all lines and fittings through which fresh, hot acid flows. Those through which only hydrolyzate flows are made of 316 stainless steel.

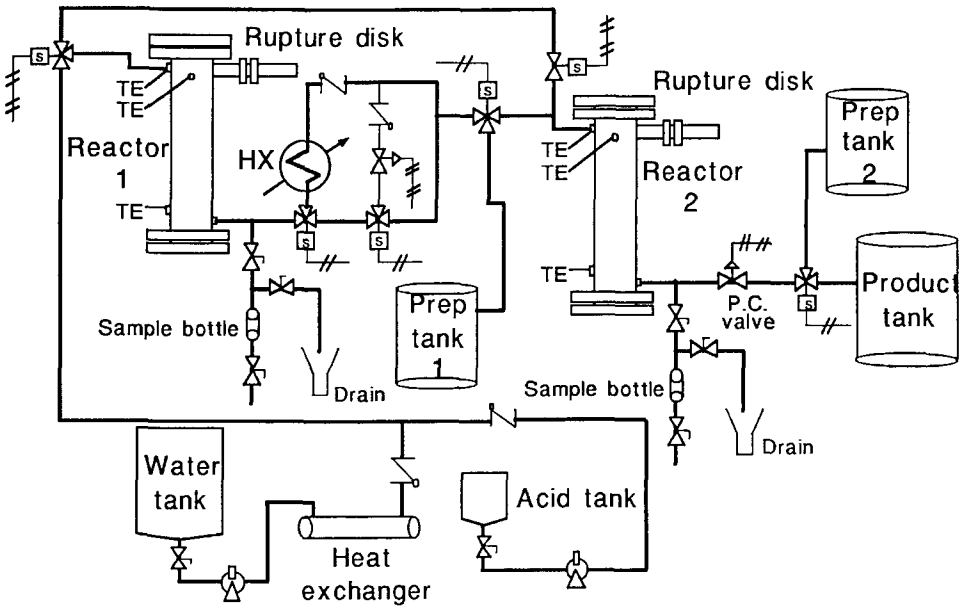

Fig. 1. Schematic of the tandem reactor experimental system.

Prior to the introduction of hot acid into a reactor, the reactor is preheated externally for 30 min via the steam jacket, then internally for 20 min by sweeping steam under pressure through the woodchip bed. Once preheating is completed, hot acid is introduced near the top of the reactor and percolates down through the bed of chips, filling the reactor. This takes from 6 to 15 min, depending on the acid flow rate and the extent of liquid saturation of the chips. Once full, the reactor pressure increases until the setpoint is reached. At this time, the product valve in the exit line near the bottom of the reactor opens enough to maintain reactor pressure and permit product flow to the rest of the system.

When a multireactor system is operated continuously, the cycle time is calculated by dividing the solids residence time, which is the same for each reactor, by the number of reactors on line. This defines how often a new reactor with fresh chips is brought on line. At the same time, the reactor at the opposite end of the train, which has been on line the longest, is taken off line (*see* Fig. 1). When continuously operating two reactors in series with a 2-h solids residence time, the reactor switch occurs at 1-h intervals.

Our tandem reactor experiments simulate continuous operation using a total run time equivalent to three cycle times. During the first cycle, reactor one (R1) is operated alone with its product directed to an auxiliary tank (Prep Tank 1 in Fig. 1). The product from R1 is sent through reactor two (R2) during the second cycle and on to the main product tank. Reactor 2 is operated alone during the third cycle with fresh acid being diverted

around R1 to R2, and its product is sent to Prep Tank 2 (*see* Fig. 1). Cycle 1 is used to bring the chips in R1 to the proper state of conversion for cycle two. Steady-state operation is simulated in cycle two, and cycle three is used to bring the chips in R2 to a similar level of conversion as the chips in R1.

As shown in Fig. 1, the choice of flow path is made by operating several air-actuated, three-way solenoid valves. A number of interstage options were built into the system. The product from R1 can be sent through the pressure control valve to Prep Tank 1 or to R2 when R2 is being filled; it can be set to R2 through a heat exchanger for heating or cooling; or it can be sent to R2 directly. In all of the experiments reported here, R2 was filled by routing the R1 hydrolyzate through the R1 pressure control valve until R2 came up to pressure. For the remainder of cycle 2, the R1 hydrolyzate was sent through the heat exchanger to compensate for interreactor heat losses. Samples can be taken at the exit of R1, near the entrance to R2, and at the exit from R2. Integration of the glucose concentrations over time in the R1 exit samples taken throughout an experiment allow the calculation of R1 product yield and concentration. The performance of R1 can thus be compared with the steady-state, cycle 2 results.

Kinetics Experimental Apparatus

The kinetics experiments were carried out in standard 8 mm diameter borosilacate glass tubing. Individual ampoules were made by cutting the tubing into 15 cm lengths, glassblowing shut one end, and coning the other to facilitate loading of the material to be tested into the ampoule. For wood hydrolysis tests, the ampoules were loaded with 0.4 gs of −60 mesh aspen wood flour and 3 mL of 0.5 wt% sulfuric acid. The weights of wood and acid were measured using a Mettler 163 digital analytical balance. The open end of the ampoules were flame sealed shut, allowing about 3 cm of free space for thermal expansion during the experiment. The ampoule design was tested to 3725 kPa absolute (540 psia) without bursting by plunging one loaded with water into a 245°C sand bath for several minutes followed by quenching in a water batch.

Up to eight ampoules could be suspended from a metal rack and lowered into the sand bath held at the temperature of interest. Pairs of ampoules were extracted and quenched at timed intervals, and the contents were analyzed to determine the composition of the liquid phase. An apparatus was constructed to allow remote control of the movement of the metal rack. The apparatus consisted of a traveling overhead crane with an electromagnet at the end. The crane was raised or lowered and moved left or right using pulleys located behind a plexiglass safety shield.

The transient thermal response of the ampoules after immersion was determined using a finite difference analog for the transient radial temperature distribution in a composite cylinder. The convective heat transfer coefficient used in the model was found experimentally to be 2043 kJ/h/m/°C (100 BTU/h/ft^2/°F) for the fluidized sand bath. The rise in tem-

perature from ambient to the 180–190°C range of interest took approximately 1.5 min. The model was verified using a water-filled metal ampoule with a thermocouple inserted into it. Measurements using a thermocouple probe indicated that: the temperature at a given location in the bath could be controlled to ±0.5°C; the spatial variation in the bath was ±0.25°C; and the initial temperature drop of the bath after immersion of a full rack of ampoules was less than 1°C.

ANALYTICAL METHODS

The hydrolyzate samples were analyzed using a Beckman HPLC with two refractive index detectors. One detector was connected to a Bio-Rad HPX-87P column for determination of sugar concentrations, and the other to a Bio-Rad HPX-87H column for determination of sugar degradation product concentrations. This HPLC configuration was also used for the analysis of the liquid products generated by the kinetics experiments.

EXPERIMENTAL RESULTS

Tandem Reactor

Presented in Table 1 are the results of five tandem reactor experiments which were done to judge the performance of a two-reactor vs a one-reactor system. Since the best results for the previously investigated single-reactor system were obtained using a hydrolysis temperature of 185°C and an acid concentration of 0.5 wt%, these values were used for all of the tandem reactor experiments.

Table 1 lists three different prehydrolysis strategies for the five experiments. In experiments T1 and T2, the raw chips were prehydrolyzed at the beginning of each reactor's first cycle by introducing the acid stream at or near 150°C through the first 25 min of product flow time. To reduce the on-line time spent at temperatures too low to produce much glucose, this strategy was changed in experiments T3, T4, and T5. In experiment T3, R1 was filled with 150°C acid and held for 25 min before coming on line. R2 was filled with cool 1 wt% acid and heated internally and externally with steam before coming on line during cycle 1. As a result of inadequate heating, the R2 prehydrolysis temperature reached only 125°C. In experiments T4 and T5, both reactors underwent the same prehydrolysis strategy as was used in experiments T1 and T2. However, the chips in R1 and R2 were prehydrolyzed the afternoon previous to the day of the experiment. After prehydrolysis, each reactor was drained and the prehydrolyzed chips were left in the reactor overnight. The next day the experiment was started at hydrolysis temperature (185°C).

Experiments T1, T2, and T3 were all done with 1.27 cm chips and a 15 min nominal liquid residence time per reactor to facilitate comparison of

Table 1
Experimental Conditions and Results from the Tandem Reactor Experiments

Experiment	T1	T2	T3	T4	T5
Prehydrolysis strategy	In line, 25 min flow at 150°C	In line, 25 min flow at 150°C	Fill and hold at 150°C for 25 min, then drain	Prehydrolyzed the day before	Prehydrolyzed the day before
Nominal liquid residence time per reactor, min	15	15	15	22.5	22.5
Cycle time, min	90	75	55	70	60
Chip size, in	<1/2	<1/2	<1/2	<1/2	<1/4
Chip dry weight R1, R2, g	2384,2457	2538,2653	2470,2541	2494,2393	2449,2450
Cycle 1 glucose, g	371	352	450	491	345
Cycle 2 glucose R1, total, g	270,456	367,623	198,414	152,484	311,479
Cycle 3 glucose, g	205	411	279	145	212
R1 stand-alone yield (%), concentration (g/L) and Mg	55.0,3.9, 215	58.0,4.6, 267	53.6,5.9, 316	52.7,6.9, 363	54.8,7.9, 433
Cycle 2 yield (%), concentration (g/L), and Mg	38.5,6.7, 258	49.0,8.3, 407	33.8,8.6, 291	40.5,9.9, 401	40.0,12.6, 479

the cycle 2, steady-state results with the best results obtained from the previously completed single reactor experiments. Cycle times of 90, 75, and 55 min were used in these experiments to cover a reasonable range of solids residence times. However, there were temperature-related problems in experiments T1 and T3. In experiment T1, a higher than expected heat loss between the two reactors and a slower than expected heatup time for R2 combined to increase the temperature ramp (prehydrolysis to hydrolysis) time from 22 min for R1 to 59 min for R2. This combined with a greater production of glucose from R1 during cycle 1 than during cycle 2 resulted in the low cycle 2 glucose yield and concentration. During experiment T3, the low prehydrolysis temperature caused a less effective prehydrolysis that, in turn, slowed down the initial hydrolysis process in R2. An effective R1 prehydrolysis caused an R1-cycle 1 glucose production far greater than the R1-cycle 2 production. As with experiment T1, the result was a poor performance from cycle 2.

Experiment T2 ran very smoothly, with both reactors undergoing very similar temperature profiles. Consequently, the glucose production from both reactors was reasonably high during cycle 2. As a result, the best cycle 2 yield of the series of experiments and the second-best value for Mg, the figure of merit (yield × concentration), were achieved. However, the cycle 2 yield is still 9% lower than the R1 stand-alone yield. Both the yield and figure of merit for cycle 2 are lower than the combination of 55% yield and 425 value for Mg achieved in the single reactor study under similar conditions (185°C, 0.5 wt% acid, and 30 min total, nominal liquid residence time).

When the R1 stand-alone yields are compared to the 55% single reactor yield, it is apparent that doubling the liquid velocity through a single reactor did not significantly increase the yield out of that reactor. This indicates that the hydrolysis process is limited by phenomena within the chip—reaction and/or diffusion—or that reactor hydrodynamics may be worsening (i.e., increased channeling). In either case, slowing down the flowrate may improve the performance of the reactor by increasing the glucose concentration without affecting the yield for the former hypothesis or increasing both for the latter hypothesis.

In experiments T4 and T5, the flowrate was reduced by 50%. Also, a smaller chip size was used in experiment T5. These changes were an attempt to alter the controlling mechanism from within the chip to one external to it. As seen in Table 1, neither strategy improved the yields on either a R1 stand-alone or cycle-2 basis. The concentrations did increase but not enough to surpass the highest figure of merit of 580 achieved in the single reactor study when 0.635 cm chips were used. The highest single reactor yield reached was 61% with a value of 441 for the figure of merit.

Kinetics Experiments

The laboratory kinetics experiments investigated the kinetics of coupled aspen hydrolysis-glucose decomposition reactions and isolated glucose decomposition reactions. The effect on both of metal corrosion products, primarily chromium ions, from the attack of acid on 316L and CA20 type stainless steels was also determined.

As shown by Saeman (*4*), the acid hydrolysis of wood can be represented by two consecutive, first-order reactions

$$\text{Cellulose} \overset{k1}{\rightleftharpoons} \text{Glucose} \overset{k2}{\rightleftharpoons} \text{Decomposition Products}$$

From this model, the concentration of glucose as a function of time can be expressed in terms of the rate constants as follows

$$\frac{G}{Gp} = \frac{k_1}{k_1 - k_2}\left(e^{-k_2 t} - e^{-k_1 t}\right)$$

where G_p is the glucose potential of the feedstock.

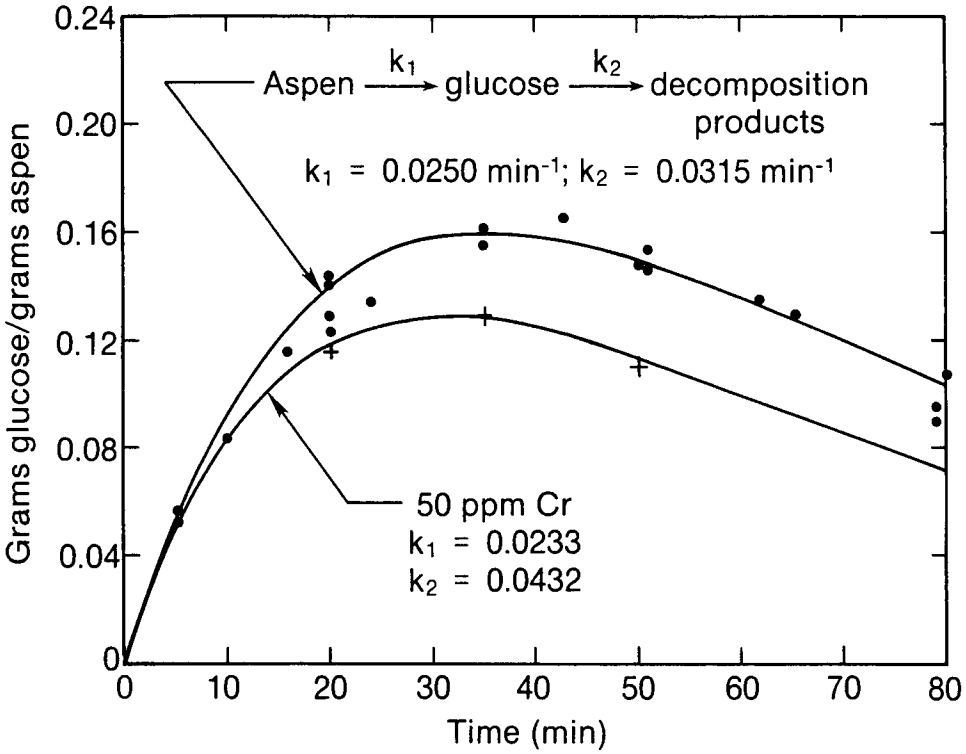

Fig. 2. Yield of glucose as a function of time for hydrolysis of aspen at 190°C in 0.5 wt% sulfuric acid (liquid/solids=7.6–7.9).

Further work by Connor et al. (*5*) has refined this simple model to account for reversion products of glucose and acid neutralization by ash in the wood. These effects are not considered in this analysis since they are second order at the hydrolysis conditions and glucose compositions involved in this study.

Saeman presented data for aspen, but did not indicate the species used or the condition of the wood (e.g., moisture content). For this reason, we reinvestigated the coupled glucose production-degradation kinetics with the wood used in the tandem reactor experiments. Values for k_1 and k_2 were obtained at three temperatures with the above equation using yield data at two different times from the aspen hydrolysis experiments. Multiple points at any one time were averaged. These average yields for each time were combined to calculate a series of k's that were, in turn, averaged to get the values of k_1 and k_2 for each temperature. The upper curve in Fig. 2 was obtained for 190°C from values of k_1 and k_2 arrived at in this manner using the points shown. This was done for 179, 185, and 190°C, and the k_1 and k_2 values were plotted as a function of inverse temperature to determine the preexponential factor and the activation energy for the glucose formation and decomposition reactions. These plots are shown in Fig. 3.

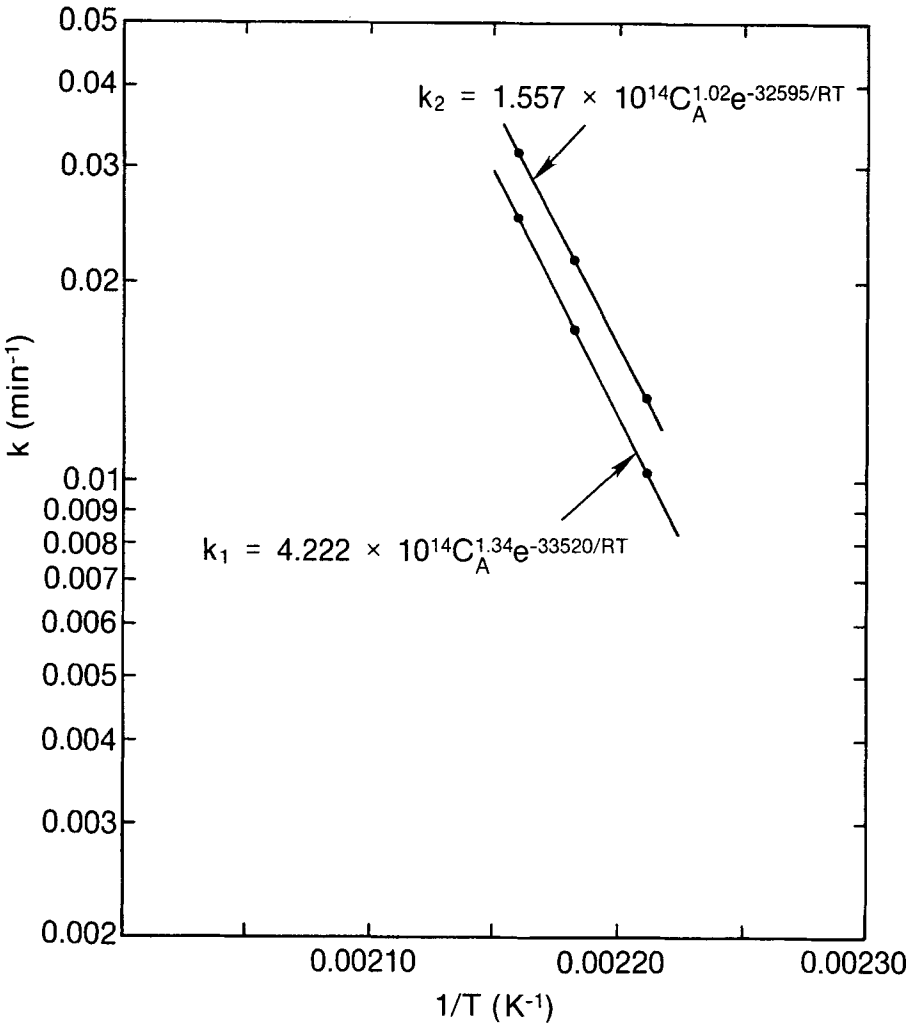

Fig. 3. Arrhenius plot for hydrolysis of aspen and decomposition of glucose in 0.5 wt% sulfuric acid.

The kinetics of glucose decomposition were investigated separately to compare them to the kinetics determined in the presence of wood and to see if metal surfaces or metal ions have a catalytic effect. Interest in the effects of metal arose when samples of hydrolyzate from the tandem reactor experiment were found to contain 25–50 ppm chromium ions as well as other ions expected from the corrosion of stainless steel. Smith (*6*), using 200°C and 1.5% acid, reported significant increases in the glucose decomposition rate in the presence of chromium ions starting at approximately 50 ppm. Nickel, copper, and iron ions were also investigated, but found to be of minor, if any, importance. Degradation tests without chromium were done at 170, 180, and 190°C. Tests using 25, 50, and 100 ppm (parts per million) chromium ions were done at 180 and 190°C. The Arrhenius

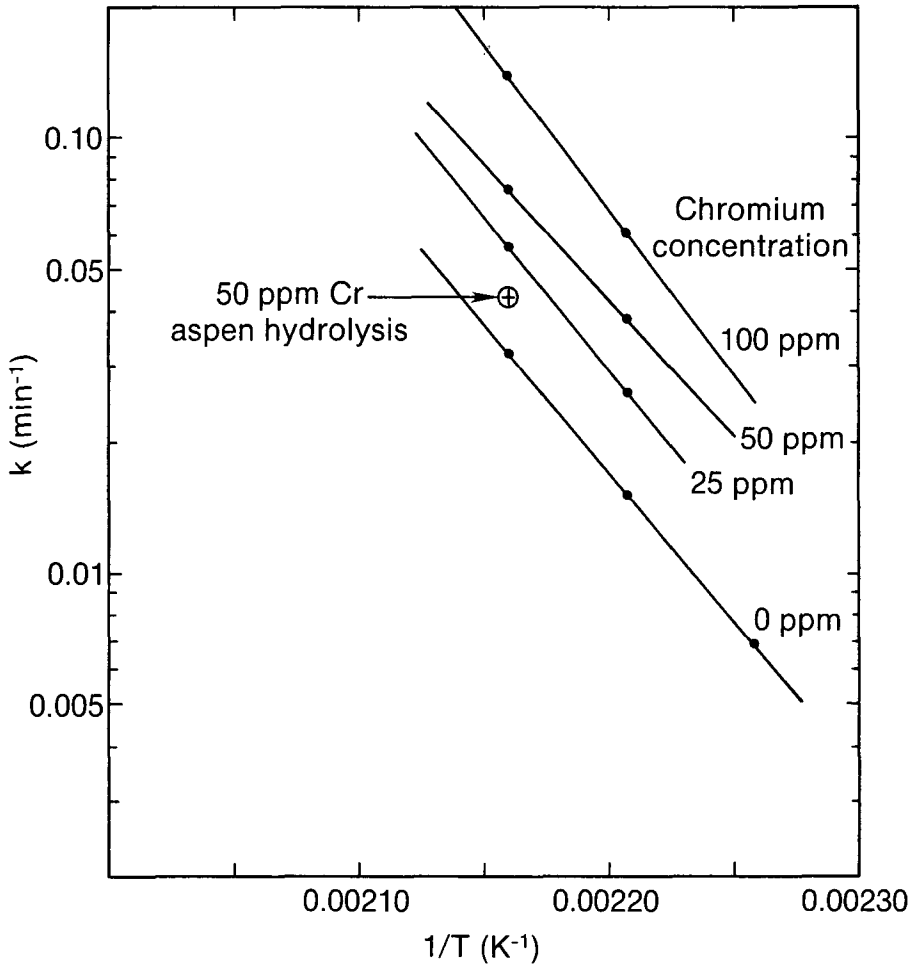

Fig. 4. Arrhenius plot for glucose decomposition in 0.5 wt% sulfuric acid with and without chromium sulfate.

plots for these tests are presented in Fig. 4. The effect on yield is presented in Fig. 2.

Additional tests were done wherein strips of 316L were placed in ampoules loaded with glucose-acid solutions and cooked. The same was done with strips of CA20. The results of these tests are displayed in Table 2. Chromium levels from the 316L quickly rose to 150 ppm and leveled off at 200 ppm, whereas the CA20 produced only 5 ppm after an additional 8 min of exposure. A greater than sevenfold increase in the degradation rate was observed with the 316L with the very high chromium ion levels. However, the rate still increased 50% over the control for the ampoules with CA20, despite the very low concentration of chromium ions.

Hydrolyzate samples containing 25 ppm of chromium from the tandem reactor experiment were also cooked to determine their glucose decomposition kinetics. In a final experiment aspen wood plus acid spiked with 50 ppm of chromium were used. These tests were performed to determine

Table 2
Results of Glucose Degradation Tests Run at 190°C and 0.5 wt% Acid with Metal Strips Inserted in the Ampoules

Metal	Sample time (min) initial–final	k_2, min^{-1}	Chromium ion concentration, ppm	k_2, with metal/without metal
None	0–32	0.036	—	1.0
CA20	24–32	0.054	5	1.5
316L	8–16	0.163	150-200	4.5
316L	16–24	0.268	200	7.4

Table 3
Comparison of Glucose Decomposition Rate Constants for 0.5 wt% Acid and 190°C

Test	Rate constant, min^{-1}	Ratio to baseline
1. Acid-glucose	0.0318	1.00
2. Acid-glucose, 25 ppm Cr	0.0561	1.76
3. Acid-glucose, 50 ppm Cr	0.0764	2.40
4. Acid-glucose, 100 ppm Cr	0.138	4.34
5. Hydrolyzate[a]	0.0611	1.92
6. Acid-Wood, 50 ppm Cr[b]	0.0432	1.36

[a] Originally contained 10 g/L glucose and 25 ppm Cr.
[b] Glucose generation rate constant of 0.0250 min^{-1}, calculated from the data.

if there are any mitigating effects on the metal ion enhanced decomposition kinetics when wood or the various wood hydrolysis products are present in solution. Rate constants calculated from the results of these tests are presented in Table 3. From test 5 in Table 3, it is evident that hydrolyzate products have little effect on the chromium enhanced kinetics. However, in the presence of wood (test 6), the rate constant for the degradation reaction drops from 0.0764 to 0.0432 min^{-1} with 50 ppm of chromium in solution.

DISCUSSION OF RESULTS

Tandem Reactor

From the preceding discussion, it is obvious that the R2-cycle 2 glucose production levels are sensitive to the relative heatup rates of the two reactors. If R1 underwent a faster heatup time than R2, cycle 2 performance suffered. However, even when the temperature histories of the two reactors were evenly matched, as in experiment T2, the cycle 2 yield

Table 4
Glucose Yields, Concentrations, and Figures of Merit Derived from the Idealized Computer Model for Hydrolysis at 185°C and 0.5 wt% Acid, and a Solids Residence Time of 90 Min

Case	Number of reactors	Liquid residence time, min	Yield, %	Concentration, g/L	Mg
1	1	7.5	74	8	592
2	1	10	71	10	710
3	1	15	65	14	910
4	1	30	53	23	1219
5	1	45	44	28	1232
6	2	30	61	25	1525
7	3	30	62	27	1674
8	4	30	63	27	1701
9	1	21	61	18	1098
10	1	39	48	25	1202

was lower than that achieved with either R1 on a stand-alone basis or the single reactor experiments.

A simple, idealized percolation reactor model that ignored glucose diffusion out of the chips was used to investigate this phenomenon. The effect of liquid residence time (t_1) on system performance predicted by this model is shown in Table 4. For the single reactor system, yield increases and final concentration decreases as the liquid residence time decreases, as seen in cases 1–5 of Table 4. For the same t_1 of 30 min, the tandem reactor system yield with t_1 equal to 15 min per reactor is predicted to be 8% higher and concentration to be 2% higher than the single reactor system. When compared to the 15 min-single reactor system, there is a 4% loss in yield to be balanced against the almost doubled concentration.

Also illustrated in Table 4 is the prediction based on the results of the idealized model of essentially unchanged performance for the PBR system with more than two active reactors on line. Since hydrolysis costs increase with number of reactors, a train with two active reactors is predicted to be economically optimum for a PBR system. Cases 6, 9, and 10 in Table 4 list the results of the computer program when the liquid residence time in a single reactor system is adjusted to produce first the same yield and then the same concentration as the optimum PBR system as another way of demonstrating the inherent superiority of the PBR concept in the ideal case. Whether the gain in either yield or concentration is sufficient to economically justify the higher costs of a PBR system depends on the magnitude of the cost differential and its impact on ethanol selling price.

This analysis can be generalized to compare the performance of a PBR system to that of a single reactor system. As long as increasing the flowrate through one reactor increases the yield from that reactor, then improvements in yield can be gained with similar concentrations by using a

multireactor PBR system with the same total liquid residence time as the alternative single reactor system. However, the PBR yield advantage is taken away if factors are present that eliminate the beneficial effects on yield of increasing the flowrate. In this case, the single reactor system will produce a higher yield when run at a liquid residence time that is the same as the per-reactor liquid residence time for the PBR system; that is, at the upper limit of flowrate.

There are two nonideal phenomena that will result in an upper limit being placed on the range of acceptible flowrates. The first is intraparticle diffusion and the second is hydrodynamics. When the hydrolysis process in a percolation reactor is controlled by the rate of intraparticle diffusion, then increasing the flow rate past that point does not improve yield noticeably but only decreases the product concentration. Since the R1 standalone yields seen in the tandem reactor experiments are approximately the same as yields from the single reactor experiments despite the twofold increase in flowrate, the process appears to be in the diffusion controlled regime.

The size of chip for which diffusion becomes the rate limiting step can be estimated using the Thiele modulus (*7*), which is defined as

$$\mathrm{TM} = L/2\,(k_2/D_e)^{0.5}$$

where

k_2 = glucose decomposition rate
D_e = glucose effective diffusivity
L = chip length

A Thiele modulus greater than 0.5 identifies diffusion as the rate limiting step. For a Thiele modulus less than 0.5 the reaction rate is the rate limiting step, and in this case the percolation reactor model without diffusion becomes plausible. We determined experimentally the effective diffusivity of glucose through aspen chips for 25, 50, and 75°C. Extrapolation of that data to 185°C yields a value of 6.9×10^{-5} cm^2/s. Using that along with an experimentally determined value of 0.0432 min^{-1} for $k2$ and setting the Thiele Modulus to 0.5 results in a chip length of 0.31 cm (0.12 in). This, although not definitive, points toward the diffusion limited regime for the single and tandem reactor experiments conducted to date.

The chip size can be reduced to switch the rate limiting step from intraparticle diffusion to liquid flowrate. However, during the single reactor experiments, system performance was found to deteriorate when <0.318 cm ($<1/8$ in) chips were used as compared to <0.635 cm ($<1/4$) in chips. Also, the results were less repeatable and predictable when chips smaller than <1.27 cm ($<1/2$ in) were used. This was attributed to hydrodynamic problems (e.g., channeling) that might be encountered in beds of smaller chips. Another problem that may arise when liquid flowrates are increased is that of excessive pressure drop and, therefore, high power costs. Very high flowrates may also lead to reactor plugging because of bed compac-

Table 5
Comparison of Rate Constants from the Present Study and the Saeman Study

Temperature, °C	k_1-Saeman, min^{-1}	k_1 min^{-1}	k_2-Saeman, min^{-1}	k_2 min^{-1}
180	0.0107	0.0112	0.0145	0.0144
185	0.0180	0.0168	0.0215	0.0214
190	0.0299	0.0250	0.0318	0.0315

tion. Wood chip beds normally shrink as hydrolysis procedes and the chips lose their structural strength. Either the reactor or downstream equipment may plug if excessively high flowrates worsen bed compaction or increase the amount of particulate matter washed from the reactor.

Kinetics

From the original kinetics study done by Saeman (4), the formation of glucose from the hydrolysis of aspen is described by

$$k_1 = 1.35 \times 10^{19} A^{1.34} \exp(-42900/R\,T)$$

and the degradation of glucose is described by

$$k_2 = 2.03 \times 10^{14} A^{1.02} \exp(-32830/R\,T)$$

where

A = acid concentration in wt%
R = 1.987 cal/mol-K
T = reaction temperature in K

As a first guess, the same simple dependence on acid concentration was assumed for our study. Saeman determined the expression for glucose degradation from experiments on glucose–acid solutions, and then used that expression with the data from his wood experiments to generate his glucose formation expression. Values of the two rate constants from Saeman's expressions are listed with our values in Table 5. Since this comparison shows the two sets of equations to be nearly identical, the acid dependence assumption was not investigated.

Results from the tests investigating the effect of chromium ions on glucose degradation kinetics, summarized in Table 3, indicate a marked increase in rate in the presence of these ions. When the chromium enhanced kinetics were investigated in hydrolyzate solutions (test 5), the degradation rate was found to be similar to (9% higher) the very high rates found for the glucose–acid–chromium ion solutions. However, when wood is present (test 6) the increase in degradation rate drops from 140 to 36% for chromium ion concentrations of 50 ppm. The k_1 value for the wood was determined to be relatively unaffected since it was calculated to be 0.0233 vs 0.0250 min^{-1} found without the chromium ions.

These results indicate the ameliorating effect to be attributable to the wood rather than any of the myriad products of wood hydrolysis found in hydrolyzates. As noted in Table 2, the presence of CA20 metal strips in the glucose–acid solutions generated only 5 ppm chromium, but still increased the degradation rate by 50%. This may indicate a catalytic effect on glucose degradation by the surfaces of certain metals. More data will be needed to ascertain the nature of the metal and metal ion catalysis.

The glucose degradation data can be used to look more closely at the relative performance of the two reactors in the tandem reactor experiment. The following assumptions must be made: first, the hydrolyzate from R1 contained 25 ppm of chromium ions (25 to 50 ppm were found in the samples tested for chromium); second, the liquid residence time from the sampling port of R1 to the sampling port of R2 was 9 min (calculated using known system volumes and flowrates for $t_1 = 30$ min); and the relative increase in $k2$ found for the hydrolyzate sample at 190°C can be applied to $k2$ found at 185°C without chromium. This leads to the calculation of 68.6% of the glucose from R1 surviving the trip through R2. If this is applied to experiment T2 (*see* Table 1), then R1 contributed 252 g of glucose to the cycle 2 total. This means that R2 contributed 371 g in cycle 2, and R2 had a stand-alone yield of 60% compared to 58% for R1 on a stand-alone basis. Even though the performances of the two reactors were balanced and both contributed evenly to the steady-state glucose production, the steady-state yield calculated from cycle 2 data was only 49% with a glucose concentration of 8.3 g/L and a figure of merit of 407.

The comparable single reactor experiment produced a yield of 55%, a concentration of 8.4 g/L (adjusted for differences in reactor charge weights), and a figure of merit of 462. Thus, as a result of nonideal conditions in the reactors, the PBR system loses its predicted advantage over the equivalent single reactor system.

CONCLUSIONS AND RECOMMENDATIONS

There were problems in a number of experiments associated with the time–temperature profiles of the two reactors that penalized the performance of the system during cycle 2, the steady-state cycle. This overreliance on system behavior during one cycle could be eliminated by adding more reactors to the train to allow a more continuous operation while still operating two reactors at a time. System performance with more than two reactors on line could also be investigated. However, the results obtained from those experiments wherein the temperature profiles of the two reactors were well matched indicated that there were two nonideal phenomena limiting the performance of the system to levels well below that predicted for an ideal system. The first of these was intraparticle glucose diffusion and the second was chromium ion catalysis of the glucose degradation reactions.

Experimental results have shown that reducing particle size to minimize intraparticle effects may introduce hydrodynamic problems that adversely affect reactor performance. A program was initiated with the aim of finding hardware modifications and/or operational strategies that might eliminate the problem. This program should be continued and expanded to investigate the practical upper limit to liquid flowrate in a large-scale reactor, since the potential improvement of a PBR system over a single reactor system depends on the rate controlling mechanism being external to the chips, and this may require high flow rates.

The problem of chromium ion catalysis of the glucose degradation reactions needs to be addressed in order to determine how much it affects the comparison of two reactor to single reactor performances. It also affects how well the data can be used to predict large-scale performance. In large-scale systems, acid brick lined reactors and teflon lined pipe could be used to prevent the generation of chromium ions. This is not possible at the scale of this experiment, but there are options available that should be investigated. Solutions that include certain pyrophosphates have been shown to inhibit corrosion of metal by acids since the surfaces of the metal objects become passivated when treated with the pyrophosphate solutions. Experiments should be done to determine the effectiveness of the various passivation techniques under the conditions encountered in the tandem reactor experiments. There may also be chemicals that complex with chromium ions and thereby render them unavailable as catalysts. If this is unsuccessful, the portion of the system that is constructed of 316ss parts could be replaced with CA20 parts—an expensive alternative.

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