0273-2289/88/1800-0251/$02.00

Experimental Studies of the Progressing Batch Reactor

Scientific Note

PAUL W. BERGERON,* JOHN D. WRIGHT,
AND PAMELA J. WERDENE

Solar Energy Research Institute, 1617 Cole Blvd., Golden, CO 80401

Index Entries: Acid hydrolysis; percolation reactor; woodchips; chip size; hydrodynamics.

INTRODUCTION

The development of the Progressing Batch Reactor (PBR) concept has been presented previously (*1,2*). In brief, the progressing batch hydrolysis reactor operates on the principle that a continuous reactor can be approximated by several batch reactors in series. The solids are processed batchwise in each reactor, while the liquid containing acid and sugar flows continuously from one reactor to the next. A reactor is taken off line at one end of the train when the woodships it contains are sufficiently hydrolyzed. It is rewplaced by a reactor with fresh chips at the opposite end of the train. Since the acid–sugar solution moves in the opposite direction to the apparent motion of the woodships, a countercurrent reaction scheme is simulated without the necessity for continuously moving solids into and out of a pressure zone, and all solids handling is done at ambient temperature and pressure.

The experimental program to investigate the potential of the PBR concept has been organized into three phases. This paper discusses the completion of the first phase, in which a single percolation reactor was operated. In this phase, the baseline data were obtained for comparison to the upcoming multireactor experiments. Even though other experi-

---

*Author to whom all correspondence and reprint requests should be addressed.

ments have been conducted with similar equipment, they have not been run at the scale of this study, with the feedstock of interest, or in the configuration deemed desirable for the PBR concept. The second phase of the study will investigate the performance of a system with two reactors operated in series, and the issues of wood chip pretreatment, interstage processing, and overall system control will be examined. The resolution of these questions is important to the design of the final experiment of the study, the six reactor system, and to the design and, therefore, economics of a full-scale process. The second phase data will also provide a preliminary indication of the merits of the PBR concept.

MATERIALS AND METHODS

The reactor was constructed of a 15 cm (6 in.) diameter, 0.9 m (3 ft)-long Carpenter 20 Cb-3 pipe with carbon-steel lap joint and blind flanges. It 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 were also constructed of Carpenter 20 Cb-3.

In a typical run, the lignocellulosic feedstock is loaded into the reactor through the top flange. For the runs reported here, the feedstock is aspen wood (*Populus tremuloides*) with the composition shown in Table 1. Three chip size ranges were used for comparison—those that passed through a 0.5, 0.25, and 0.125 in. screen. The moisture content of the chips was approximately 5%.

Table 1
Chemical Composition of Aspen Wood Feedstock

	% Anhydrous 45 ° oven dried basis	% Anhydrous bone dry basis	% hydrated[d] bone-dry basis
Glucan[a]	43.0	44.3	49.1
Galactan[a]	.4	.4	.4
Mannan[a]	1.1	1.1	1.3
Xylan[a]	15.2	15.7	17.3
Arabanan[a]	.9	.9	1.0
Klason lignin[a]	21.0	21.6	21.6
Ash[b]	.3	.3	.3
Acetic anhydride[b]	3.1	3.2	4.5
Glucuronic anhydride[b]	3.2	3.3	3.6
Water[a]	3.0	—	—
Other (extractives)[c]	8.8	9.2	9.2
	100	100	108.3

[a] Results of analysis done at SERI.

[b] Average values from *The Chemical Technology of Wood* by Hermann Wenzl.

[c] Remainder necessary to add up to 100 except for hydrated, bone-dry basis.

[d] Takes into account the water added to the original molecule in order to better define the potential weight of the final product expected from that fraction of the wood charged to the reactor.

At the start of a run, the reactor vessel is preheated externally with steam at approximately 150°C for 30 min. Following this, the wood chip bed is swept with steam at 140–150°C for 20 min to remove air from the bed and preheat the chips. Air is removed to facilitate acid penetration into the chips. A dilute acid mixture (<1% sulfuric acid) is then injected near the top of the reactor at a temperature of 150°C to prehydrolyze the wood. It takes approximately 20–30 min to fill the reactor, depending on the acid flowrate necessary to achieve the desired liquid residence time. Once full, the pressure quickly rises to the setpoint value of the pressure control valve, which then opens to stabilize the pressure. At this time, product begins to flow from the reactor into the product tank, which is vented to maintain atmospheric pressure. Typical reactor residence times varied from 30 to 50 min.

During prehydrolysis, the amorphous sugars (primarily xylose, arabinose, mannose, and some glucose) and the acetic and glucuronic acids are converted into soluble products. When the time alloted for prehydrolysis is up, the acid inlet temperature is ramped up to the hydrolysis value, as is the steam used for external vessel heating. A nominal hydrolysis temperature of 185°C was used in this set of experiments. The higher temperature initiates the hydrolysis of the crystalline cellulose to glucose. The cellulose hydrolysis is carried out for up to 3 h. Samples of the hydrolyzate are collected and cooled under pressure to ensure that all components are collected.

When the run is completed, the product valve is closed and the reactor drain valve is opened. Free liquid is flashed through this valve into a separate tank. Cold water is introduced into the top of the reactor and drained out the drain valve. The solids are then removed from the reactor, weighed, dried, and then reweighed. Two or three 5–10 g samples are taken of the wet solid residue for analysis of lignin content. The hydrolyzate samples are analyzed by an HPLC using a Bio-Rad HPX-87P column for determination of the sugar concentrations.

EXPERIMENTAL RESULTS

Work done prior to that reported here (*1*) was confined to the acid hydrolysis of 1/2 in. chips in a single, downflow percolation reactor with woodchip packing densities averaging approx. 2500 dry g/reactor vol (g/v). The standard prehydrolysis routine included filling the woodchip-packed reactor with acid at 150°C (approx. a 25 min fill time) followed by a 25 min period during which the 150°C prehydrolysis temperature was maintained. The acid feed temperature was then raised to the chosen hydrolysis level and left there for the duration of the experiment. Variations in hydrolysis temperature, liquid residence time, acid concentration, and solids residence time were studied. Results were compared on the basis of glucose yield and glucose concentration in the product.

A figure of merit, M_g, was calculated by multiplying the yield by the concentration. This facilitates both the determination of the stop time for hydrolysis for each experiment, and comparisons among the various experiments. The best results were achieved using a nominal hydrolysis temperature of 185°C, a nominal liquid residence time of 30 min, and an acid concentration of .5 wt%. These conditions produced a yield, concentration and M_g of 60%, 6.4 g/L, and 384, respectively, when data from the full 155 min hydrolysis time was used in the analysis. Shortening the hydrolysis time to 109 min changed these values to 55%, 7.8 g/L, and 425.

The latest single-reactor experimental results are presented in Tables 2 and 3. In these Tables, variations caused by differences in the amount of dry wood charged to the reactor and differences in the hydrolysis time are eliminated. Each sugar concentration is divided by the ratio of the dry wood charged in the experiment to the average dry wood charge.

Once hydrolysis begins, the instantaneous concentration of six-carbon sugars in the product stream rises to a peak and falls off as the reaction proceeds. The optimum time to terminate the process is determined by comparing the economic benefit of producing more six-carbon sugars with the economic detriment of reducing the sugar concentration as the product sugar concentration continues to fall. Since this is a decision based on plant economics, most of the experiments were run well past the optimum termination time. The sugar production data are easily adjusted back to the optimum termination time by subtracting the weight of sugars produced after this time from the total sugars produced. The liquid volume is also adjusted by subtracting the liquid pumped through the reactor after the optimum termination time from the total liquid pumped through the reactor during the experiment. The adjusted sugar weight is then divided by the adjusted liquid volume to find the new final concentration for the adjusted run time. The time at which the glucose concentration fell to approximately 3–4 g/L was used as the adjusted termination time. Figure 1 illustrates typical profiles of the cumulative values of glucose concentration and yield along with the resulting figure of merit.

Reactor performance is sensitive to temperature profile when operating near the optimum temperature region (185–188°C). In a number of experiments the temperature ramp from prehydrolysis to hydrolysis temperatures overshot during 15 min or so of the hydrolysis time. For the same nominal hydrolysis temperature, these experiments with the temporary temperature overshoot performed better than those without (see Experiments 2 and 12 in Table 2). The experiments with temperature overshoot are noted in Table 2, and only those experiments with similar temperature histories are compared.

In experiments 12, 20, and 22, 1/2-in., 1/4-in., and 1/8-in. chips, respectively, were used to demonstrate the effect of particle size on glucose yield and concentration. As the particle size is reduced, the chip surface area increases and the time required by the glucose molecules produced

Table 2
Results from Liquid Downflow Experiments All Run at 185°C Nominal Hydrolysis Temperature and 0.50 wt% Sulfuric Acid

Experiment	2	12	20	22	23	15	16	18	19
Temperature ramp profile	OSB[a]	—	—	—	OSB	OSB	OSB	—	—
Liquid residence time, min	29.3	29.7	29.6	29.3	29.5	29.7	40.1	39.9	39.9
Chip size, in	½	½	¼	⅛	¼	½	¼	¼	¼
Dry charge, g	2384	2403	2504	2651	3011	2502	2992	2565	2695
Prehydrolysis time, min	52	50	48	50	52	30	35	56	70
Temperature ramp time, min	15	22	35	37	30	17	26	25	40
Hydrolysis time, min	109	106	122	101	106	114	101	113	143
Glucose concentration, g/L	7.8	7.0	7.2	7.1	6.4	8.4	9.8	8.6	9.1
Glucose yield, %	55	50	61	54	45	50	56	48	57
Mg	425	350	441	381	288	420	550	416	519

[a] OSB temperature overshoot at reactor bottom.

Table 3
Results from Liquid Upflow Experiments All Run with 30 Minute Liquid Residence Time and 0.5 wt% Sulfuric Acid

Experiment	24	25	26	27
Hydrolysis temperature, C	185	185(OSB)[a]	185	180
Liquid residence time, min	29.2	29.4	29.0	29.4
Chip size, in	½	¼	½	½
Dry charge, g	2078	3093	2047	2283
Prehydrolysis time, min	49	49	49	49
Temperature ramp time, min	13	32	14	15
Glucose concentration, g/L	6.9	6.6	6.3	5.9
Glucose yield, %	40	45	41	46
Mg	278	295	258	271

[a]OSB = temperature overshoot at reactor bottom.

within the chip to diffuse out of the chip decreases. Although wood chip preparation costs increase as particle size decreases, the reduction in glucose diffusion time could reduce product degradation and, therefore, pay off in higher yields. As can be seen in Table 2, however, the best results were attained with the 1/4-in. chips. Values for glucose yield and M_g of 61% and 441, respectively, were realized for the 1/4-in. chips and only 54% and 381, respectively, for the 1/8-in. chips. This seems to indicate an

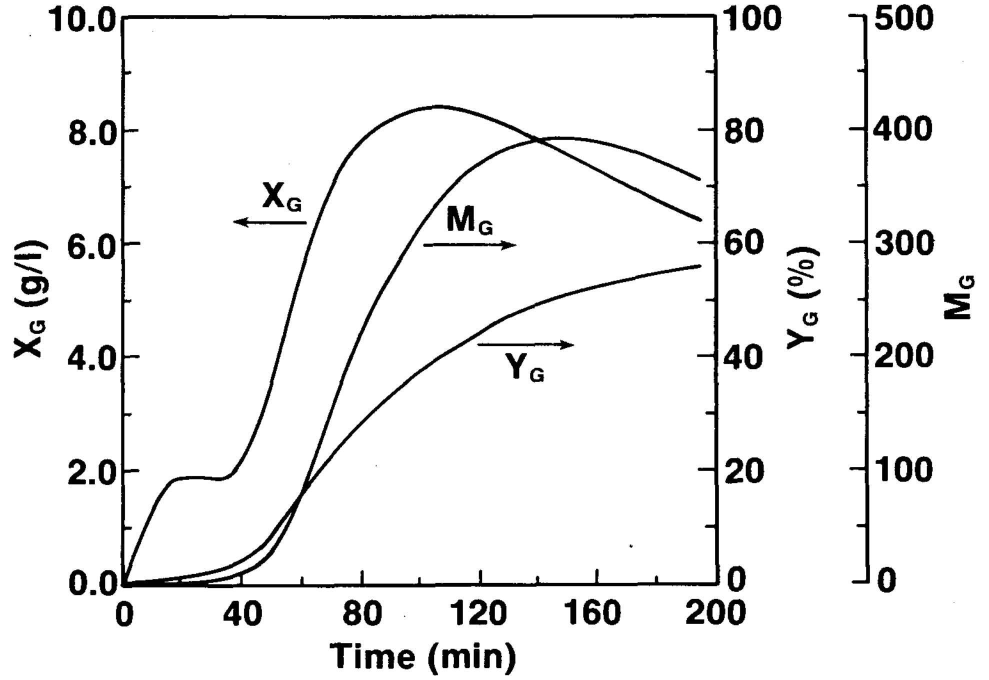

Fig. 1. Typical profiles of the values of the glucose concentration in the product (X_g), the glucose yield (Y_g), and the resulting figure of merit ($M_g = X_g \times Y_g$).

adverse change in the interparticle hydrodynamics within the reactor for the smallest chips. The total glucose residence time in the reactor is the sum of that in the chip and that in the free stream. If the smaller chips cause more liquid channeling, the effect could be to increase, rather than decrease, the average glucose residence time.

The interaction of bed hydrodynamics with chip packing density was also investigated. If packing density has no effect on hydrodynamics, then packing more chips into the reactor should increase the product concentration while leaving the yield unchanged. Using 1/4-in. chips, the packing density was raised from 2500 in Experiment 20 to 3000 dry g/reactor vol (g/v) in Experiment 23. This caused a dramatic reduction in performance as shown by the drop in values of M_g from 441 to 288 and yield from 61% to 45%, respectively, in Table 2. This was the case despite the more advantageous temperature profile indicated for Experiment 23.

The consequence of increasing packing density was not, however, straightforward. This aspect was seen in three experiments performed to study different prehydrolysis strategies. In Experiments 15 and 16, rather than maintaining prehydrolysis temperatures through the first 25 min of product flow, the temperature was ramped up to the hydrolysis level immediately after the reactor was filled and pressurized. In Experiment 16, 1/4-in. chips packed to a density of approximately 3000 g/v were used. Instead of seeing a drop in performance as in Experiment 23, the yield and figure of merit, M_g, reached 56% and 550, respectively, this M_g being the highest attained for the single reactor experiments. Experiment 15 was performed using 1/2-in. chips packed to the lower density of 2500 g/v. Reactor performance was not improved, but was nearly identical to the control run in which the standard prehydrolysis procedure was used (Experiment 2). Substituting a no-flow, hold time at prehydrolysis temperature for the standard flow time and using 1/4-in. chips at an intermediate packing density of 2700 g/v in experiment 19, again resulted in a significant increase in reactor performance as evidenced by the values of 520 for M_g and 57% for yield.

Since a bed of unhydrolyzed 1/2-in. chips is much less compressible than one composed of 1/4-in. chips, the range of packing densities is much smaller for the 1/2-in. chips. The variability of reactor performance with packing density and prehydrolysis procedure observed with 1/4-in. chips was not observed for 1/2-in. chips. The bed hydrodynamics for 1/4-in. and smaller chips may depend on the wood chip packing procedure and chance variations in chip size distribution.

Finally, Experiments 24 through 27 were performed in the liquid upflow mode to investigate the effect of bed height behavior and the possibility of improving reactor hydrodynamics. However, our bed of hardwood chips has consistently been observed to have shrunk to approximately 25% of the original height at the end of each downflow experiment. In the upflow mode, this would cause the bed to shrink away from the reactor exit. The shrinkage of the wood chip bed for the upflow experiments was found to be very similar to that for the downflow experiments. The upshot of this is an increasing sugar residence time in the space above the chips as the bed shrinks. The data from the upflow experiments presented in Table 3 confirms this to be the overriding consideration in upflow hydrolysis. In all four experiments the values of M_g were below 300, and yields ranged from 40 to 46%. Only Experiment 25 compared favorably with its downflow counterpart–the 1/4-in. chip, high packing density Experiment 23. This experiment produced almost identical values of M_g and yield as the downflow Experiment 23 that performed so poorly relative to the other downflow experiments. The similarity of performance is assumed to be a result of the variability in reactor performance when using the smaller 1/4-in. chips.

DISCUSSION

These experiments conclude the initial phase of the PBR program. The primary objective of this phase was to provide a sound baseline for comparison of the results to be obtained from the multireactor experiments. Data from the single reactor, 1/2-in. chip experiments provide such a reliable baseline. These data are not sensitive to wood chip packing procedures nor to prehydrolysis strategies, as are the data from the experiments using smaller chips. The use of wood chip sizes smaller than 1/2-in. may improve reactor performance enough to justify the additional expense in the chip preparation section. However, the combined effects of wood chip size and packing density on bed hydrodynamics needs further study.

The inferior performance of the reactor in the upflow versus the downflow configuration highlights a potential problem for the multireactor system because of the shrinking bed phenomenon. The height of a wood chip bed and, therefore, the void volume fraction in each of a series of reactors at any time will be determined by the extent of hydrolysis in each reactor at that time. The residence time of liquid through an empty portion of a reactor is much higher than that for a wood chip-filled portion. Consequently, the average residence time for sugar molecules produced in a reactor train can be much higher for a series of liquid-filled, shrinking-bed reactors than for reactors with constant void volume fractions. The extent of the problem associated with bed shrinkage depends on the as yet unknown rate at which the bed shrinks.

With information on bed hydrodynamics, improvements in reactor design and/or operating procedures can be developed to eliminate potential problems associated with the use of a series of percolation reactors to hydrolyze woodchips.

CONCLUSIONS AND RECOMMENDATIONS

The data obtained in the single reactor experiments has shown the use of 1/2-in. chips to produce results that are reliable and repeatable.

These data are not sensitive to variations in wood chip packing or prehydrolysis procedures. The latter is important since multireactor studies will try various prehydrolysis strategies while investigating the operational characteristics of a multireactor system.

The possible importance of hydrodynamics within the wood chip bed was demonstrated by the data from the 1/4- and 1/8-in. chip experiments. The importance of shrinking wood chip bed was demonstrated by the reactor's inferior performance in the upflow versus the downflow mode. A hydrodynamic study should be undertaken to investigate these phenomena. This study can proceed concurrently with work on a two-reactor system that can give a preliminary glimpse at the operation and benefits of a multireactor system.

REFERENCES

1. Bergeron, P. W., Wright, J. D., and Werdene, P. J. (1986), "Progressing Batch Hydrolysis Reactor Single-Stage Experiments," Eighth Symposium on Biotechnology for Fuels and Chemicals, No. 17, pp. 33–51.
2. Wright, J. D., Bergeron, P. W., and Werdene, P. J. (1987), I & EC Research, **26,** 699.