Comparison of the Pretreatment of Sweetgum and White Oak by the Steam Explosion and RASH Processes

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ABSTRACT

Steam explosion and rapid steam hydrolysis/continuous extraction (RASH) processes were compared using sweetgum and white oak as the feedstocks. Both pretreatments employ steam and are relatively rapid, but there are several differences between the two processes. Both pretreatments dramatically increased the enzymatic hydrolysis rate but not the acid hydrolysis rate of the cellulose. Both water insoluble xylose or alkali insoluble lignin contents could be used to predict the relative enzymatic hydrolysis rate. Steam explosion depolymerized and degraded the hemicelluloses, whereas RASH minimized further degradation of the hemicelluloses. The lignin was depolymerized by both pretreatments, with steam explosion forming a moderately condensed lignin. No significant differences were observed between white oak and sweetgum samples treated by either process, suggesting that the selection of particular hardwood is not a critical factor for a potential biomass plant in the southeastern US.

Index Entries: Steam explosion; rapid steam hydrolysis; biomass pretreatment; white oak; sweetgum.

INTRODUCTION

In the last 15 years the need to find alternative sources of energy and chemicals has led to extensive research efforts to develop economical processes for converting agricultural, forestry, and municipal wastes into fuels and chemicals. Proposed enzymatic processes for making ethanol

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from lignocellulosic materials usually involve three major steps: a pretreatment step to partially break down the biomass; a hydrolysis step to convert the polysaccharides into monosaccharides; and a fermentation step to convert the monosaccharides into ethyl alcohol. Acid hydrolysis processes often do not include a pretreatment step, although a pretreatment that reduces the cellulose crystallinity would be beneficial. The primary purpose of the pretreatment is to disrupt and break down the lignin and holocellulose polymers and thus increase the accessibility of the cellulose to enzymatic hydrolysis. In other words, the pretreatment should increase the rate and the extent at which the cellulose is hydrolyzed to glucose. In addition, the pretreatment should utilize inexpensive chemicals and capital equipment and solubilize and fractionate the lignin and hemicelluloses so that these components can also be commercially utilized.

Another important characteristic of a pretreatment is that it must be effective with an inexpensive, but available, biomass material. Many pretreatments are very dependent on the type of feedstock used. A review of past research will show that a large amount of biomass research has been conducted on aspen. Millett et al. (1) and Lipinsky (2) have both noted that aspen is a uniquely easy wood to pretreat and that aspen only grows in limited northern regions of the US. Thus, promising results obtained using aspen do not necessarily indicate that the pretreatment will be successful with other woods. In addition, hardwoods are generally more susceptible to pretreatment than softwoods. In the southeastern US the feedstock of choice would probably be mixed hardwood chips obtained by total-tree chipping of small diameter, low quality hardwoods (the so-called trash species). The two major hardwood species growing on southern pine sites are sweetgum (*Liquidambar styraciflua* L.; 13.2% of total hardwood volume) and white oak (*Quercus alba* L.; 12.3%) (3). These two hardwoods have different physical properties. Sweetgum is a medium density, diffuse-porous wood, whereas white oak is a high density, ring-porous wood. In addition, white oak has about twice the extractives as sweetgum (4) and is reported to be about five times as acidic as sweetgum (4,5). Finally, the cells of white oak heartwood are filled with tyloses, which impede the flow of water.

Steam Explosion

The steam explosion process was originally developed by Mason in 1925 and has been extensively used in the manufacture of hardboard. In 1978 the Iotech Corporation, Ltd., of Canada started using this process for the production of ruminant feed. In view of the early results that showed the high digestibility of steam-exploded wood, Iotech decided to explore the use of this process as a method for pretreating aspen and other feedstocks (6,7).

Since Iotech first reported their initial results, other investigators have also studied the steam explosion process as a biomass pretreatment for

hardwoods and for agricultural wastes. These investigators have found that the following chemical changes occur during steam explosion (6–20)

1. The lignin is broken down into products with a molecular weight range of from 150 to 7000. These products, which retained the basic lignin structure, were reported to be highly reactive and have been examined as a partial phenol replacement in adhesives. Since the lignin is extensively depolymerized by cleavage of the ether bonds, it is partially soluble in alkaline solutions or certain organic solvents.
2. The hemicelluloses are partially broken down and are predominantly soluble in hot water. In addition, some degradation products are formed that apparently condense with lignin, thereby increasing the apparent lignin content.
3. Steam explosion causes a large increase in the accessibility of the cellulose to enzymatic hydrolysis, but not to acid hydrolysis. In addition, the degree of polymerization (DP) of cellulose is greatly reduced. Early reports suggested that the explosion was necessary to increase enzymatic hydrolysis rates (6,7,10, 11,13), but more recent studies have shown that explosion is not necessary (20–23).
4. Aspen and some other feedstocks gave high yields, but relatively low yields were reported when oak was used as a feedstock (7).

Rapid Steam Hydrolysis/Continuous Extraction

The Rapid Steam Hydrolysis/Continuous Extraction procedure, called RASH, is similar to the steam-explosion process. Unlike the steam-explosion process, however, soluble or gaseous products are continuously removed from the reaction zone and cooled, thus minimizing further degradation. Also, the RASH treatment does not have the physical explosion step. The RASH treatment was developed in order to compare the effect of a chemical treatment (steaming) alone vs a dual chemical and physical treatment (steaming and explosion) (17,24). The RASH process has been studied utilizing mixed hardwoods and red oak (17,24,25). This work has shown that

1. The hemicelluloses are hydrolytically depolymerized and extracted from the biomass with minimal degradation;
2. The lignin is also hydrolyzed, and up to 95% can be extracted by aqueous alkali or organic solvents;
3. The remaining solid residue is considerably enriched in cellulose;
4. The enzymatic hydrolysis rate of the cellulose increases dramatically, and thus the explosion portion of the steam explosion pretreatment is not necessary; and

5. Little or no increase in the rate of acid hydrolysis is observed.
   Similar results have also been reported when hardwoods were
   steamed (26,27).

Although both processes have unique differences, either pretreat-
ment can be easily modified. For example, a steam explosion gun can be
modified to remove condensate (6) and the steam can be gradually re-
leased without the explosion (21,22). These modifications essentially will
give the RASH process.

The objective of this study was to compare two biomass pretreatment
processes (steam explosion and RASH) and two potential biomass feed-
stock sources from the southeastern US region (sweetgum and white oak).

METHODS

Green sweetgum and white oak bolts were debarked, cut into quar-
ters on a bolter saw, and chipped to standard size pulp chips. The green
chips were stored in a cold room until used.

The Masonite steam explosion reactor has been previously described
(15-17). The pulp-sized chips were exploded using a one minute heatup
time and a reaction time of 1 min. The thermocouple broke during the
runs and subsequent temperatures were estimated by measuring the re-
action pressure and correlating the reaction pressure to the reaction tem-
perature of previous runs in which mixed hardwood chips were exploded.
The exploded fiber was air-dried, ground, and stored in a refrigerator
prior to analysis or hydrolysis experiments. The cyclone used to separate
the wood fiber from the steam was not designed for high pressure runs.
Thus, a significant portion of the wood fibers was lost out of the top of
the cyclone, with the result that the material balances could not be deter-
mined.

Prior to the RASH pretreatment, the chips were air-dried then ground
using a 6-mm mesh. Thus, the chip size for RASH runs were smaller than
those used for the explosion process. All fines less than 2 mm size were
removed from the 6-mm chips. A 600 mL Parr reactor was used as the re-
actor vessel. The reactor setup and operation have been described earlier
(17,24). The reactor typically reached the desired temperature in about 30
s, and required about 40 s to cool down. The reaction time was 1 min.

The analysis procedures used are described below. All analyses were
done in duplicate with the average reported, except where noted.

1. The procedure for analyzing the solids and condensate for
   Klason lignin, soluble lignin, and carbohydrate content have
   been reported earlier (15,24). The yield of galactose was not

determined. White oak is reported to contain 1.1% galactan and sweetgum less than 1% (4).

2. The solid samples were extracted with hot water or refluxing 2% aqueous alkali, as described earlier (15,17).

3. The RASH-pretreated sweetgum samples were also extracted with acetone at room temperature, with the extracted fiber then filtered and washed with an excess of distilled water. The extracted samples were then air-dried and analyzed.

4. The nitrobenzene oxidation procedure was performed at 160°C for 3 h (28). A temperature of 160°C instead of 175°C was used by mistake. The results are based on the weight of aldehydes formed per weight of available lignin in the fiber. The lower temperature will result in a reduced yield of about 30%.

5. The enzymatic hydrolysis procedure is the same as described earlier (16,17,24). The RASH-pretreated solids were hydrolyzed directly, while the steam-exploded samples were extracted with hot water prior to enzymatic hydrolysis. The water extraction was performed in order to make the samples as comparable as possible. Since the pretreated solids had different amounts of cellulose, the percent glucose formed was based on the total available glucose.

6. The acid hydrolysis procedure was similar to the procedure described earlier, except a hydrolysis temperature of 85°C was used instead of 105°C (16,17). The steam-exploded fiber was extracted with hot water prior to acid hydrolysis. The percent glucose formed was based on the total available glucose.

RESULTS

Table 1 gives the chemical analysis of sweetgum chips that were steam exploded for 1 min, and Table 2 shows the analysis of exploded white oak chips. *Analysis of water- and base-extracted samples was based on the pretreated, nonextracted fiber, in order to clearly show the extent to which each wood component was extracted.*

Table 3 gives the RASH conditions and solids recovered, and the analysis of the RASH solids is shown in Table 4. The RASH condensate analysis is reported in Table 5. *The results on the extracted RASH solid samples are also based on the nonextracted fiber.*

The total aldehyde yield from the nitrobenzene oxidation is given in Fig. 1 for both RASH and steam exploded samples. The relative enzymatic hydrolysis rates are shown in Fig. 2, and the acid hydrolysis rates in Fig. 3.

Table 1
Analysis of Sweetgum Chips that Were Steam Exploded after One Minute Treatment

Sample	Reaction temperature, °C	Nonextracted samples[a] Yield, wt%				
		Lignin[b]	Glucose[c]	Xylose	Mannose	Arabinose
Control	—	28.1	46.1	12.9	2.7	0.3
01	211	29.4	51.2	11.5	2.3	0.3
02	222	30.9	50.6	9.3	2.0	0.2
03	230	30.9	48.4	7.4	1.7	—
04	235	35.1	52.5	5.5	1.3	0.1

Sample	% Insoluble in refluxing water	Water-extracted samples[a,d]				
		Lignin[b]	Glucose[c]	Xylose	Mannose	Arabinose
Control-WE	97.1	27.0	43.5	12.8	2.2	0.2
01-WE	79.0	21.9	46.9	5.3	1.5	0.2
02-WE	80.0	24.3	49.7	4.2	1.6	—
03-WE	77.3	24.7	49.2	2.3	0.7	—
04-WE	80.8	29.5	50.7	1.5	0.4	—

Sample	% Insoluble in refluxing 2% NaOH	Base-extracted samples[a,e]				
		Lignin[b]	Glucose[c]	Xylose	Mannose	Arabinose
Control-BE	78.6	23.0	41.5	9.0	0.7	0.2
01-BE	57.8	12.8	43.8	1.8	0.3	0.1
02-BE	53.6	9.8	42.6	1.0	0.3	—
03-BE	40.9	6.1	36.8	0.9	0.3	0.1
04-BE	34.9	3.9	31.6	0.5	0.1	—

[a]Each value is an average of two analyses.
[b]The lignin value is the sum of the Klason and soluble lignin.
[c]The glucose value is the average result determined using both the GC and glucose analyzer.
[d]The fiber samples were placed in boiling water for 1 h, with the reported values based on the starting nonextracted material.
[e]The samples were refluxed in 2% NaOH for 1 h, with the reported values based on the starting nonextracted material.

Table 2
Analysis of White Oak Chips that Were Steam Exploded after One Minute Treatment

Sample	Reaction temperature, °C	Nonextracted samples[a]					
		Lignin[b]	Yield, wt%				
			Glucose[c]	Xylose	Mannose	Arabinose	
Control	—	33.4	40.5	13.3	2.0	0.7	
10	211	35.5	44.3	10.5	1.6	0.3	
11	222	35.9	46.6	9.3	1.5	0.2	
12	230	36.0	46.7	7.7	1.3	0.3	
13	235	40.7	48.5	5.2	1.5	0.2	

Sample	% Insoluble in refluxing water	Water-extracted samples[a,d]				
		Lignin	Glucose	Xylose	Mannose	Arabinose
Control-WE	93.1	28.5	39.2	13.8	1.7	0.4
10-WE	75.6	22.0	44.5	5.2	1.3	—
11-WE	73.8	27.4	47.8	2.2	0.4	—
12-WE	75.1	28.3	46.3	1.2	0.2	—
13-WE	76.9	31.7	45.1	1.0	0.2	—

Sample	% Insoluble in refluxing 2% NaOH	Base-extracted samples[a,e]				
		Lignin	Glucose	Xylose	Mannose	Arabinose
Control-BE	77.5	23.8	39.0	10.8	0.5	0.3
10-BE	49.4	9.9	39.0	1.0	—	—
11-BE	42.0	4.7	37.0	0.6	—	—
12-BE	36.6	2.7	34.1	0.4	—	—
13-BE	30.6	1.7	29.4	0.3	0.1	—

[a] Each value is an average of two analyses.
[b] The lignin value is the sum of the Klason and soluble lignin.
[c] The glucose value is the average result determined using both the GC and glucose analyzer.
[d] The fiber samples were placed in boiling water for 1 h, with the reported values based on the starting nonextracted samples.
[e] The samples were refluxed in 2% NaOH for 1 h, with the reported values based on the starting nonextracted samples.

Table 3
Reaction Conditions Used for Pretreatment of White Oak and Sweetgum by the RASH Process

Sample	Material	Reaction temperature, °C	% Solids remaining	Condensate, mL	pH of condensate
Control	Sweetgum	—	100.0	—	—
21	Sweetgum	140	98.7	57	5.6
22	Sweetgum	160	98.7	88	5.3
23	Sweetgum	180	98.1	108	4.7
24	Sweetgum	200	93.8	188	4.1
25	Sweetgum	220	85.3	225	3.6
26	Sweetgum	240	78.6	285	3.5
27	Sweetgum	260	65.6	280	3.1
28	Sweetgum	280	51.0	365	3.0
Control	White Oak	—	100.0	—	—
31	White Oak	140	98.6	83	4.4
32	White Oak	160	97.1	96	4.4
33	White Oak	180	94.3	135	4.4
34	White Oak	200	88.2	192	3.8
35	White Oak	220	82.5	238	3.5
36	White Oak	240	75.4	290	3.5
37	White Oak	260	68.1	313	3.2
38	White Oak	280	49.9	435	3.0

Table 4
Chemical Analysis of RASH-Pretreated Solids and Extracted Solids

Sample	Material	Reaction temperature, °C	% Solids recovered	Non-extracted solids[a]			Base-extracted solids[d]			Acetone-extracted solids[e]		
				Lignin[b]	Glucose[c]	Xylose, mannose, arabinose[f]	Insoluble, %	Lignin[b]	Glucose[c]	Insoluble, %	Lignin[b]	Glucose[c]
Control	Sweetgum	—	—	30.6	45.9	19.2	81.7	23.4	43.5	98.4	24.1	41.4
21	Sweetgum	140	98.7	26.3	46.2	17.6	78.1	20.2	44.0	98.9	20.9	41.7
22	Sweetgum	160	98.7	23.9	48.4	18.3	78.6	20.6	44.2	99.2	33.5	38.6
23	Sweetgum	180	98.1	29.1	47.8	19.2	77.5	20.5	43.9	99.2	20.3	42.4
24	Sweetgum	200	93.8	27.0	49.2	18.6	71.4	20.0	45.7	99.4	26.3	43.7
25	Sweetgum	220	85.3	31.3	54.7	15.9	65.6	16.1	50.6	99.1	25.2	48.0
26	Sweetgum	240	78.6	32.3	58.6	11.9	54.5	11.2	47.8	96.6	26.0	54.7
27	Sweetgum	260	65.6	35.0	64.0	4.3	32.9	3.4	31.2	76.5	12.6	60.8
28	Sweetgum	280	51.0	40.5	65.4	2.1	30.1	2.9	29.0	69.0	10.3	59.8
Control	White oak	—	—	32.6	40.9	15.8	77.4	21.3	38.2	98.6		
31	White oak	140	98.6	31.4	42.4	16.7	80.9	22.2	42.6	98.9		
32	White oak	160	97.1	32.6	44.3	17.7	79.2	21.5	41.5	99.8		
33	White oak	180	94.3	30.8	43.4	16.3	74.9	19.1	40.4	99.5		
34	White oak	200	88.2	31.8	44.5	16.2	66.1	16.1	42.3	99.6		
35	White oak	220	82.5	33.6	49.4	14.5	58.3	13.5	42.5	99.4		
36	White oak	240	75.4	34.7	54.7	9.4	48.8	6.7	42.5	91.7		
37	White oak	260	68.1	38.0	58.5	3.8	31.5	1.5	29.5	76.9		
38	White oak	280	49.9	50.8	51.3	1.8	26.5	7.3	18.4	58.7		

[a]The values are the average of two analyses.
[b]The lignin value is the sum of the Klason and soluble lignin.
[c]The glucose value of the extracted samples was determined using only the glucose analyzer.
[d]The fiber samples were placed in boiling 2% NaOH for 1 h, with the reported values based on the nonextracted solids. The values are the result of one analysis.
[e]The fiber samples were extracted at room temperature using acetone, with the reported values based on the nonextracted solids. The values are the result of one analysis.
[f]Sum of the xylose, mannose, and arabinose.

Table 5
Analysis of the Condensate Obtained by Pretreating Sweetgum and White Oak by the RASH Process

Sample	Material	Reaction temperature, °C	% Yield, based on the starting material[a]				
			Lignin[b]	Glucose	Arabinose	Xylose	Mannose
Control	Sweetgum	—	—	—	—	—	—
21	Sweetgum	140	Tr	0.1	Tr	Tr	Tr
22	Sweetgum	160	0.2	0.2	Tr	Tr	Tr
23	Sweetgum	180	0.2	0.2	Tr	Tr	0.1
24	Sweetgum	200	0.8	0.4	0.1	0.9	0.3
25	Sweetgum	220	2.2	0.6	0.2	3.8	0.6
26	Sweetgum	240	2.6	0.8	0.1	6.0	1.0
27	Sweetgum	260	3.0	1.0	0.1	2.0	0.5
28	Sweetgum	280	4.6	1.1	Tr	0.2	1.0
Control	White oak	—	—	—	—	—	—
31	White oak	140	0.7	0.1	Tr	Tr	Tr
32	White oak	160	0.5	0.1	Tr	Tr	Tr
33	White oak	180	1.1	0.3	0.2	0.2	0.1
34	White oak	200	1.6	0.2	0.2	0.8	0.2
35	White oak	220	2.8	0.3	0.3	4.3	0.4
36	White oak	240	2.1	0.4	0.2	5.6	0.6
37	White oak	260	2.8	0.8	0.2	2.1	0.4
38	White oak	280	4.5	1.9	0.1	0.2	0.1

[a]The yield is based on the oven-dry wt of the material prior to pretreatment. Each value is the average of two analyses.
[b]The lignin content is the sum of the Klason and soluble lignin.
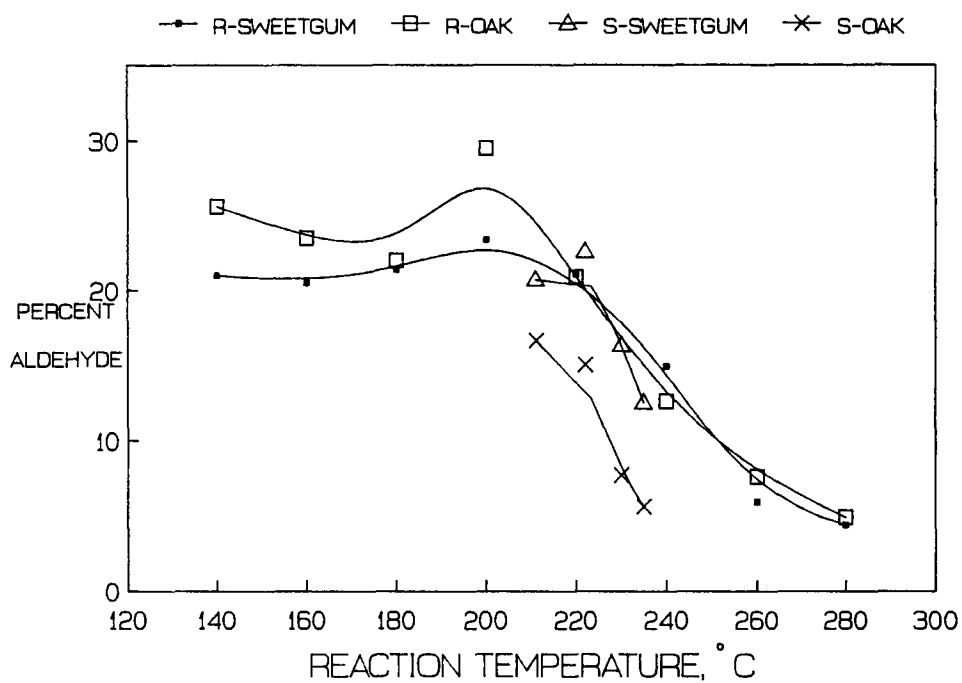
Fig. 1. Aldehyde yield following a nitrobenzene oxidation, based on the lignin content.
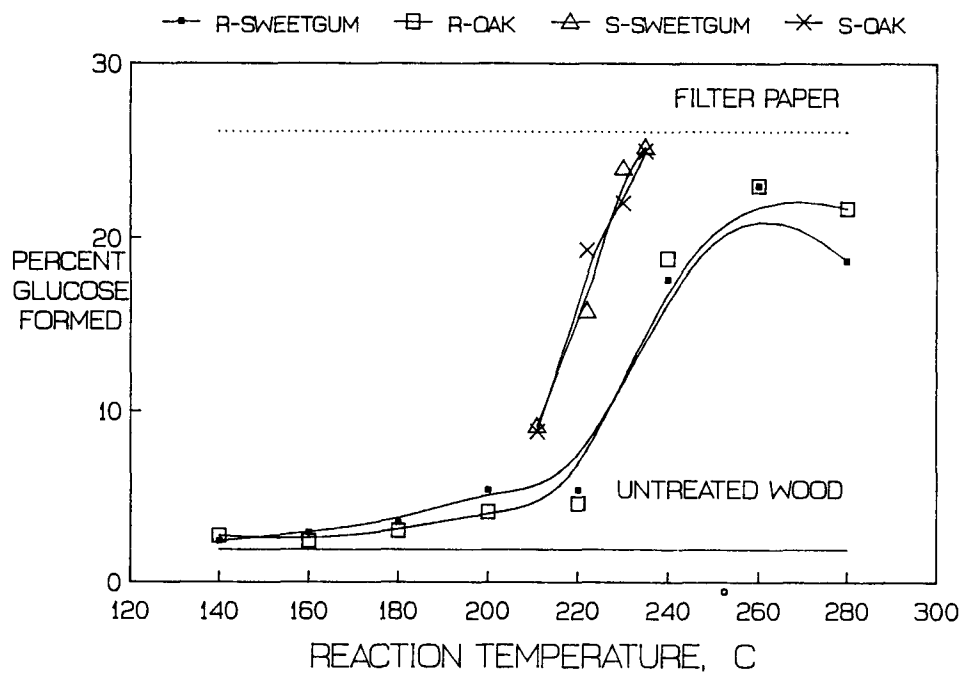

Fig. 2. Relative enzymatic hydrolysis of the treated samples based on the total available glucose. The steam-exploded samples were water extracted.
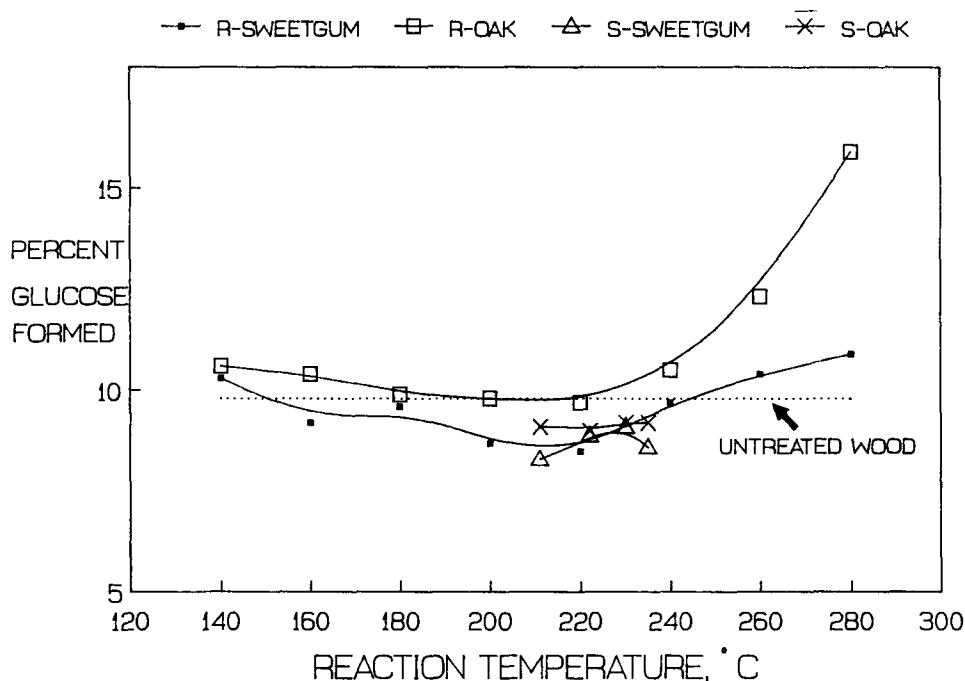
Fig. 3. Relative rate of acid hydrolysis based on the total available glucose. The steam-exploded samples were water extracted prior to hydrolysis.

DISCUSSION

At the highest steam explosion temperature of 235°C, over 50% of the hemicelluloses were degraded for both sweetgum and white oak (Tables 1 and 2). The remaining hemicelluloses were generally soluble in hot water. As expected, the lignin content increased as the reaction temperature increased. The increase in the lignin content may be partially due to the formation of so-called pseudolignin. A portion of the apparent lignin was extracted by hot water, suggesting that carbohydrate derivatives may indeed comprise some of the lignin. Extraction with refluxing 2% NaOH removed a large fraction of the lignin from the exploded fiber; 90% of the lignin was extracted from white oak and sweetgum fiber exploded at 235°C. Interestingly, only about 75% of the lignin was extracted from mixed hardwood chips exploded at 233°C (17). This may be partially owing to the presence of bark in the mixed hardwood chips, and the absence of bark in the sweetgum and white oak chips. A high proportion of polyphenolic compounds is present in bark, and this material may condense with lignin at the higher reaction temperatures to form a lignin with a higher molecular weight and consequently lower solubility. In addition to extracting lignin, the hot alkali extraction also removed a portion of the available glucose. Approximately one-third of the available glucose was extracted from both white oak and sweetgum fiber exploded at 235°C.

This solubilization of glucose has also been observed for exploded mixed hardwoods and agricultural materials (*15–17*) and is presumed to be low-molecular-weight cellulose (*8,17,26*). The alkaline extraction procedure may also have caused the peeling reaction to occur, which would further decrease the cellulose DP.

Table 3 shows the solids recovered for white oak and sweetgum pretreated using the RASH process. The yield of recovered solids decreased as the reaction temperature increased, with approximately a 50% recovery at 280°C for both sweetgum and white oak. A slightly lower solids yield was observed for white oak than for sweetgum.

Table 4 gives the analysis of solids from RASH-treated sweetgum and white oak. The reported values for samples extracted with base and acetone are based on the starting nonextracted material so that it can easily be seen which constituents and how much were extracted.

From the data in Table 4 it can be seen that the hemicelluloses were extracted during the RASH run at reaction temperatures of 220°C and above. Hot alkali extracted some lignin, with the amount of lignin removed dependent on the pretreatment temperature. For samples pretreated at 240°C or above, a significant amount of available glucose was also solubilized by the base extraction. The cellulose of white oak samples was slightly more soluble in hot alkali than the sweetgum samples. The sweetgum solids were also extracted with acetone, with the lignin not very soluble when samples were pretreated at 240°C or less (Table 4). The nonextracted, RASH-treated sweetgum solids had the highest glucose content, reaching a maximum of approximately 65%. RASH-treated white oak solids had only a slightly lower glucose content, except for the 280°C solids. Water-extracted, steam-exploded samples had a slightly lower glucose content than the RASH samples.

Table 3 also gives the mL of condensate and the acidity (pH) for the RASH runs. At the lower reaction temperatures, the white oak condensate was more acidic than the sweetgum condensate. It has been reported that oak is approximately five times more acidic than sweetgum (*4,5*). The analysis of the condensate is shown in Table 5. The yield was based on the oven-dry weight prior to the RASH pretreatment. A high proportion of the hemicellulose sugars was detected in the condensate of the 220 and 240°C runs. At the higher reaction temperatures of 260 and 280°C, the xylose content decreased. This suggests that hydrolyzed sugars were degraded at the higher temperatures in the reactor before they were extracted.

The effect of the pretreatment on the lignin in the treated solids was determined by nitrobenzene oxidation (Fig. 1). The yield of aldehydes was based on the weight of available lignin in the treated solids. Starting at about 220°C, it appears that the lignin became increasingly condensed as the reaction temperature increased. At any temperature, the lignin of steam-exploded white oak was condensed to a greater extent than the exploded sweetgum or RASH samples. Based on these results, it appears

that steam-exploded lignin is not highly reactive, as was reported earlier (7). The low reactivity is in agreement with the poor to moderate results obtained when steam-exploded lignin was used as a 30% phenol replacement in formulating a plywood adhesive (29).

Figure 2 shows the rate of enzymatic hydrolysis of the pretreated samples. The steam-exploded samples were extracted with hot water prior to enzymatic hydrolysis so that the steam-exploded and RASH samples would be similar (both containing only the water insoluble fraction). The percent glucose formed was based on the total available glucose. The average enzymatic hydrolysis rate of untreated sweetgum and white oak is shown as a solid horizontal line on the bottom of Fig. 2, and the hydrolysis rate of filter paper is shown as a dashed horizontal line near the top. The relative hydrolysis rate of filter paper is shown in order to give an indication of the maximum activity expected with the particular experimental procedure used. As the reaction temperature increased, solids from both the steam-explosion and RASH processes showed increased rates of enzymatic hydrolysis. At the highest steam-explosion temperature of 235°C, both sweetgum and white oak samples had a relative enzymatic hydrolysis rate approximately equal to filter paper. At any reaction temperature, the RASH-treated solids did not have as rapid a hydrolysis rate as did steam-exploded samples. After a 260°C RASH treatment, the hydrolysis rate of the pretreated solids approached the hydrolysis rate of filter paper.

Results from the acid hydrolysis experiments are shown in Fig. 3. Previous researchers have noted that the steam-explosion process or steaming alone did not increase the acid hydrolysis rate or decrease the cellulose crystallinity, except for steam-exploded rice hulls (8,11,13,15–18,24,26). RASH-treated samples also had no increase in acid hydrolysis except for a very slight increase for the white oak samples treated at 260 and 280°C. Prior studies suggest that the alkali solubility of the cellulose may be owing to a low cellulose DP (8,11,17,26). The steam treatment has been shown to dramatically lower the DP, but no evidence for a decrease in the cellulose crystallinity has ever been reported (11,13,18). A prior report has suggested that the amorphous regions of the cellulose may be degraded in the same manner as are the hemicelluloses by a steam pretreatment (17). This degradation of the amorphous regions would result in cellulose with a low DP but a slightly enhanced crystallinity. The slightly enhanced crystallinity would reduce the acid accessibility and result in a slightly lower rate of acid hydrolysis. Disruption of the lignin and hemicellulose network would result in the dramatically increased enzymatic hydrolysis rate observed (20). Thus, a pretreatment that will increase the rate of enzymatic hydrolysis should not be assumed to also be beneficial for acid hydrolysis.

The efficiency of any hydrolysis process, either acidic or enzymatic, is dependent on the cellulose content of the solid feedstock material prior to hydrolysis. The glucose content of alkali-extracted pretreated solids ap-
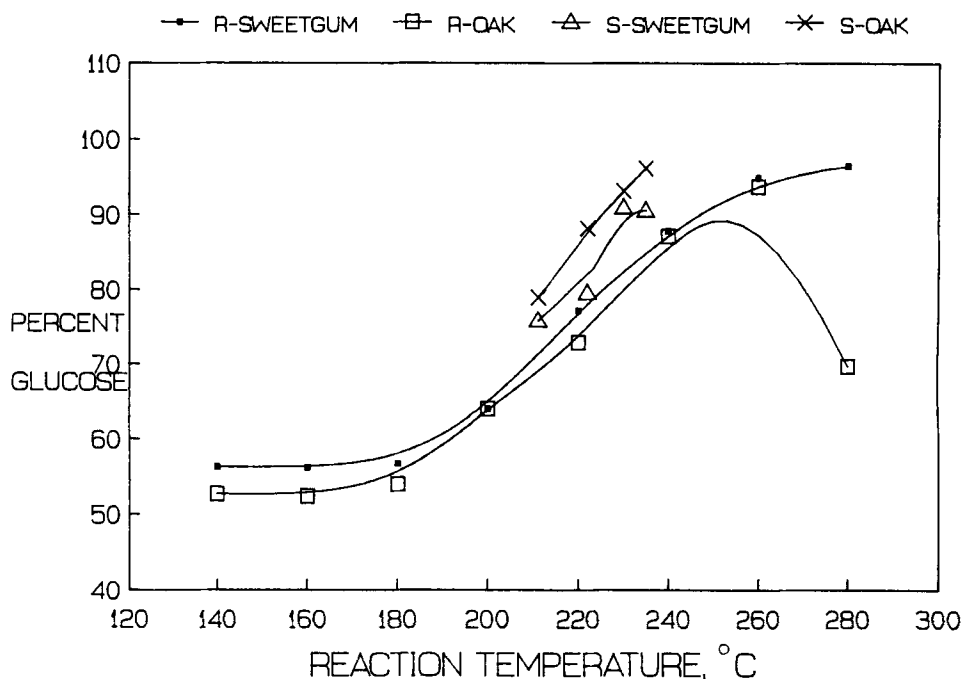
Fig. 4.   Glucose content of base-extracted solids.

proaches 100% (Fig. 4), since both pretreatments depolymerize the lignin and hemicellulose components sufficiently for these polymers to be alkali soluble. However, it is important to remember that base-extraction will also solubilize significant amounts of cellulose (Tables 1, 2, 4, and 5) for samples pretreated at the higher reaction temperature. Thus, the overall glucose yield based on material *prior* to pretreatment may be quite low.

The use of alkali insoluble lignin and residual xylan has been used as a predictor for the relative enzymatic hydrolysis rate (*30–32*). A plot of the enzymatic hydrolysis rate (as percent glucose formed) versus either the alkali insoluble lignin (Fig. 5) or the water insoluble xylan (Fig. 6) gave reasonable correlations (R^2 of 0.895 and 0.909, respectively). Surprisingly, the same regression equation appears to fit all samples regardless of the feedstock source (white oak or sweetgum) or pretreatment (RASH or steam explosion). In addition, the *y*-intercept for both Figs. 5 and 6 was approximately the value for the relative enzymatic hydrolysis of filter paper, which can be assumed to have essentially no lignin or xylan. A slightly better fit was obtained using insoluble xylan (Fig.-6). However, the alkali insoluble lignin values correctly predicted the downturn in the enzymatic hydrolysis rates at the highest RASH temperature of 280°C (Fig. 2). The authors wish to emphasize that although the insoluble lignin and xylan content can be used to *predict* the relative enzymatic hydrolysis rate, this is not proof that these factors were the direct *cause* of the increase in enzymatic hydrolysis rates. Figure 5 is evidence, however, that the
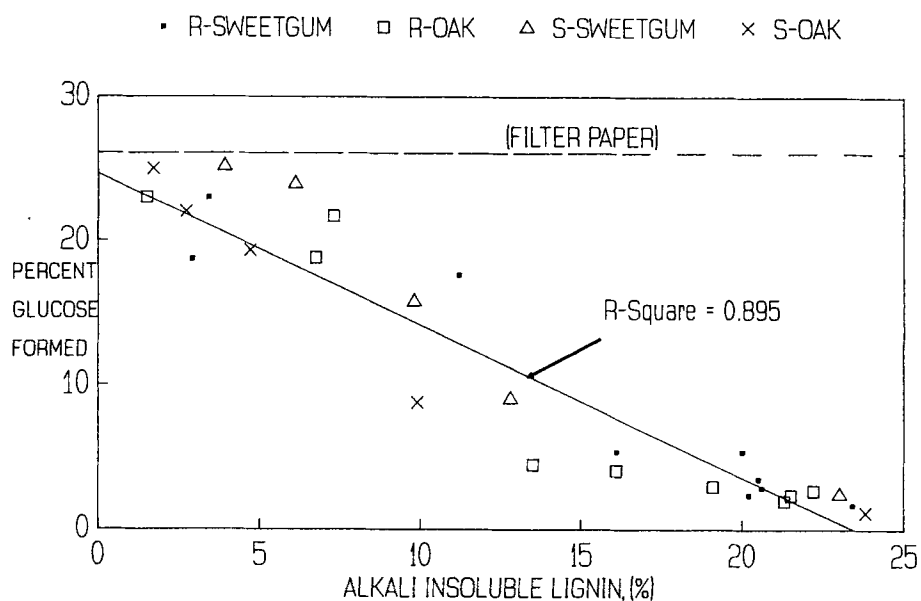
Fig. 5. Plot of the residual lignin remaining after a hot alkali extraction vs the relative enzymatic hydrolysis rate for the water-extracted steam exploded samples or the RASH-treated samples.
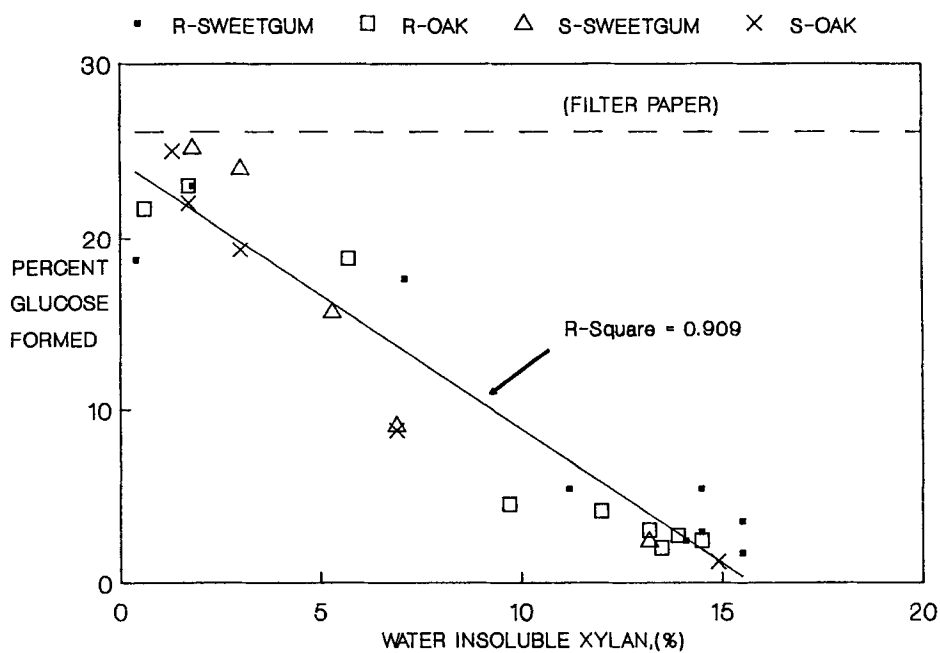

Fig. 6. Plot of the residual xylan (measured as xylose content) remaining after a hot water extraction vs the relative enzymatic hydrolysis rate.

lignin network needs only to be disrupted, not removed, for the enzymatic hydrolysis rate to be dramatically increased.

It is of interest to note that there are no significant species differences in the steam-exploded samples. This was a bit surprising since, as discussed earlier, sweetgum and white oak have significantly different physical, chemical, and structural features. No species differences were also observed with the RASH process, except at the highest reaction temperature of 280°C. The differences were: slightly higher relative rate of acid hydrolysis for oak (15.9 vs 10.9%); and a lower glucose content for oak after alkali extraction (69.7 vs 96.4%, based on alkali-extracted solids). These differences might be caused by the higher acidity of oak (4,5), which could result in more acid-catalyzed degradation.

A comparison of the two processes showed a few differences that have been previously reported (17). These are believed to be caused by slight process differences. Specifically, RASH continuously removes acidic and other water-soluble products that are trapped in the steam explosion gun. The lower relative acidity probably means that RASH products undergo slightly less hydrolytic depolymerization/degradation reactions than steam-explosion products. Thus, the RASH pretreatment results in slightly less degradation of the holocellulose components and slightly lower enzymatic hydrolysis rates than the steam explosion pretreatment.

The ''best'' pretreatment temperature is selected not on the best yield or reactivity of any one component, but on finding a compromise temperature that will optimize the factors and products of particular interest to the company that is building the biomass plant, including yields and reactivity of all the lignocellulose components. For example, selecting a reaction temperature that gives the highest enzymatic hydrolysis rate will result in low yields of hemicelluloses, some degradation of the cellulose, and an unreactive lignin.

CONCLUSIONS

No significant species differences between sweetgum and white oak samples were observed, except for 280°C treated RASH samples. As expected, both steam-explosion and RASH greatly increased the enzymatic hydrolysis rate but not the acid hydrolysis rate of the cellulose. Either water insoluble xylan or alkali insoluble lignin can be used to predict the relative enzymatic hydrolysis rate of pretreated samples. The hemicelluloses and cellulose were depolymerized, with the extent of further degradation dependent on the reaction temperature and process.

The lignin from both processes was also depolymerized. Contrary to previous studies, the steam-exploded lignin was not highly reactive and the lignin's suitability for *direct* use (no further chemical modification) as a phenolic adhesive component is questionable, especially for low-temperature cured wood composites such as plywood. However, if the pretreat-

ment temperatures were chosen such that *equivalent enzymatic hydrolysis rates were obtained*, then the exploded oak lignin would have similar reactivity as the two RASH lignins, while the exploded sweetgum lignin would be the most reactive. The reactivity of the RASH lignin was dependent on the reaction temperature.

ACKNOWLEDGMENTS

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