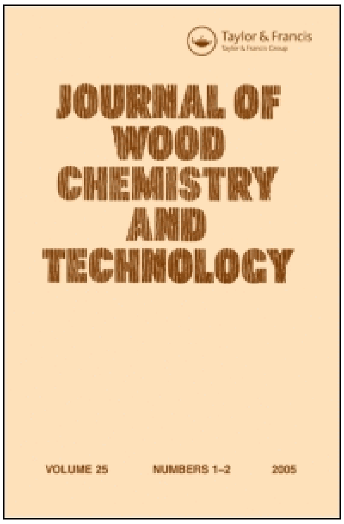

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RAPID STEAM HYDROLYSIS/EXTRACTION OF MIXED HARDWOODS AS A BIOMASS PRETREATMENT

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ABSTRACT

Rapid steam hydrolysis of wood chips with continuous condensate/product removal was investigated as a biomass pretreatment similar to steam explosion. Steam was introduced at the top of a pressurized reactor containing mixed southern hardwood chips while steam condensate and partible products were removed at the bottom of the reactor. A reaction time of one minute was employed for isothermal steaming runs from 160-280°C. Fractionation of wood occurred at temperatures above 200°C as hemicellulose and lignin began to appear in the steam condensate fraction, leaving a cellulose-rich fraction in the steaming reactor. At high temperatures cellulose was not degraded as much as it was in steam explosion at the same temperature, presumably due to the removal of acetic acid as it is formed. Lignin extracted from the solid residue appeared particularly reactive as determined by nitrobenzene oxidation and pyrolysis/gas chromatography. Lignin collected in the steam condensate was also very reactive, presumably due to its rapid cooling after being removed from the reactor.

INTRODUCTION

Biomass conversion by fermentation of lignocellulosic materials to ethanol, acetic acid, and other chemicals utilizes

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the glucose formed by the hydrolysis of cellulose. New developments in fermentation technology may also allow fermentation of carbohydrates obtained from the hemicelluloses.[1] It is important that lignin and hemicellulose be converted to useful products in order to increase the commercial viability of biomass conversion in general, since these fractions make up about 50 percent of the plant material.[2,3] Fractionation of the lignocellulosic material early in a conversion scheme benefits biomass conversion by allowing separate processing of each fraction.

The objective of a biomass pretreatment is to fractionate the wood or other lignocellulosic material as well as to reduce the high molecular weight and crystallinity of cellulose responsible for its difficult hydrolysis. Lowering the molecular weight of lignin, and partially removing it from the substrate, greatly enhances the rate of enzymatic hydrolysis of the cellulose. Removal of lignin by pretreatment before acid hydrolysis of the cellulose is beneficial because lignin subjected to elevated temperatures in the presence of acid solutions may become highly condensed and unreactive (e.g. Klason lignin).

Pretreatments such as autohydrolysis and steam explosion use only water and heat, making these processes relatively inexpensive. Additionally, if reaction temperatures and times are kept moderate, there is a minimum of carbohydrate degradation. Steam explosion, first developed by Mason in 1925, has been used extensively by the hardboard industry.[4] In 1978, Iotech Corporation Ltd. of Canada began using steam explosion to produce ruminant feed. Consequently, steam explosion is an established technology.

In the commercial process for hardboard production, a vertical cylinder is filled with wood chips and sealed. Saturated steam pressurizes the vessel up to 1000 psi for short periods of time, usually less than five minutes. During this time, chemical and physical changes occur in the wood. The bottom of the cylinder is then suddenly opened, causing defibration of the chips during their expulsion. Steam explosion of wood as a biomass pretreatment has been shown to give a highly reactive lignin with a molecular weight of 600-10,000,[5] partially depolymerize the hemicelluloses to water soluble products,[6] and increase the accessibility of cellulose to enzymatic hydrolysis.[7]

Autohydrolysis also produces low molecular weight lignin degradation products,[8] but the lignin products tend to condense by forming carbon-carbon bonds during autohydrolysis.[9] Wayman and Lora[10] found that adding 2-naphthol and other aromatic compounds during autohydrolysis aided delignification by limiting condensation reactions. Interestingly, the naturally occurring p-hydroxy benzoic acid, present as an ester, of aspen also acts as a blocking agent to lignin condensation[11] and contributes to the relative ease of pretreating this species.

The purpose of this study is to develop a method to rapidly steam wood chips (1.0 minute) with provisions to remove condensed steam along with water soluble and volatile products as they are formed. Continuous product removal and short reaction times should allow partial breakdown of the wood fractions with a relatively small amount of secondary reactions such as condensation of lignin. We have chosen the acronym RASH for RApid Steam Hydrolysis to name the process.

Low grade southern hardwood chips[12] were studied, since this material offers the best potential of woody biomass in the southeastern United States. Also, these results can then be compared to work involving other biomass conversion pretreatments carried out at our laboratory using the same material.

METHODS AND MATERIALS

Wood chips containing mostly oak and gum species were obtained from a commercial wood yard and stored according to

Schultz et al.[6] The chips were air dried, ground to pass a 6-mm screen, and the fines, less than 2 mm, which was about 15 percent of the material, were removed to prevent obstructing the steam condensate removal line. The moisture content of the 6-mm chips was approximately 15 percent prior to being added to the RASH reactor. Chemical analysis of the wood chips showed them to consist of 41-44 percent cellulose, 22-24 percent hemicellulose, and 26-28 percent Klason lignin based on the corresponding ovendry weight.

Reactor Setup and Operation. A schematic diagram of the reactor setup is shown in Figure 1. A 7.5 L Parr reactor provided steam up to a temperature of 300°C which was transferred to a 300 mL Autoclave reactor by a 1/8" OD stainless steel line. (More recent experiments have employed a 1/4" transfer line and a 600 mL Parr reactor as the reaction vessel to give faster heat up times.) A thermocouple wire connected to a digital thermometer was used to measure the temperature of both reactors. The steam condensate removal line consisted of 1/8" stainless steel tubing 1.5 meters long coiled in a bucket of cold water. The free end of the condensate line rested outside the bucket over a 1 L flask to collect the steam condensate. The other end of the condensate line extended to the bottom of the reaction vessel below a layer of glass wool, to prevent obstruction of wood chips.

In a typical run, the steam generator was set at the higher of 250° or 20°C above the target temperature in the steaming reactor. Approximately 25 grams of wood chips were placed in the steaming reactor, and the reactor sealed. The valve on the condensate line was opened slightly to allow a manageable steam flow. The valve on the steam transfer line was opened slightly, to preheat the reactor to about 105°C, and then opened completely; within 40 seconds the steaming reactor was up to temperature. The steam transfer valve was adjusted as necessary to maintain the

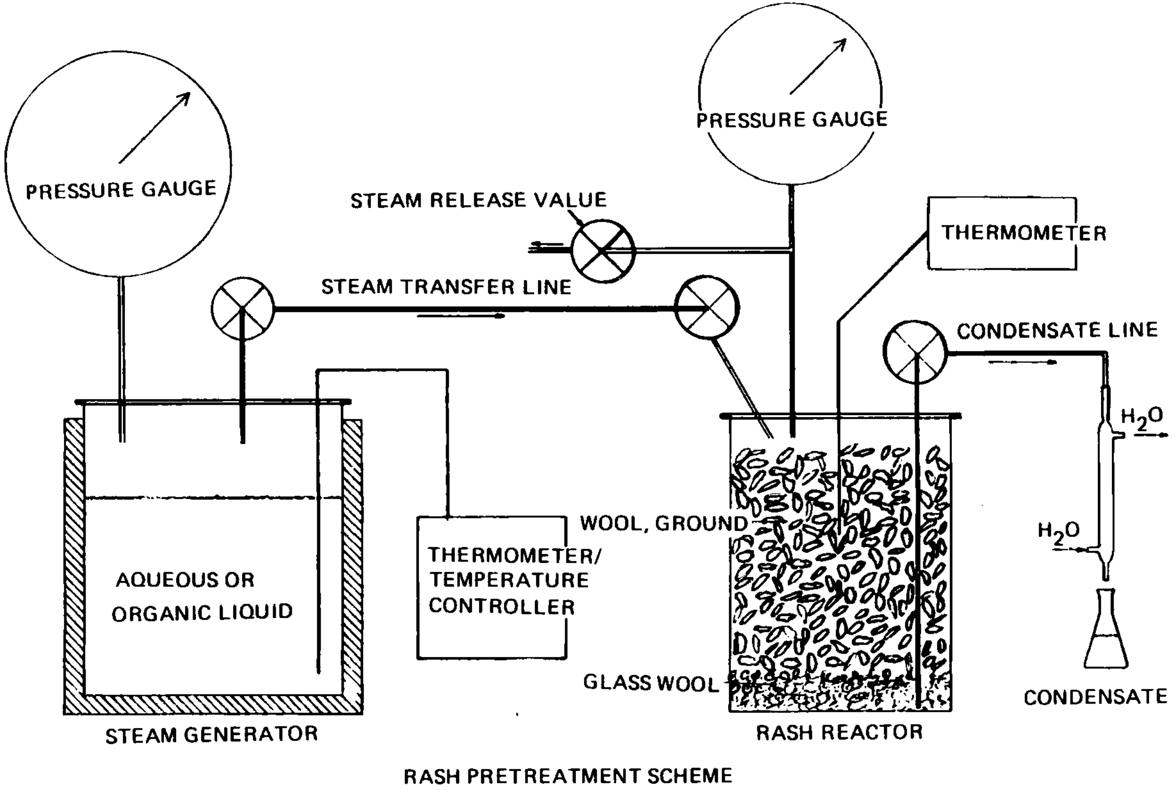

Figure 1. Schematic diagram of the rapid steam hydrolysis process for pretreatment of wood chips.

desired temperature ± 3°C for 1.0 minute. The pressure was about 90 percent of the vapor pressure of steam for the temperature of the run. Cooling was rapidly effected by closing the steam transfer valve and completely opening the steam condensate valve. Typically, 200-400 ml of steam condensate was collected for reaction temperatures of 160-280°C respectively.

Sample Analysis. The RASH separation scheme is shown in Figure 2. Prior to analysis, the solids were air dried, weighed, and ground. Moisture contents were taken before and after grinding and used to calculate yields based on the original ovendry material. The various solid portions and liquid steam condensate were analyzed for lignin, glucose, xylose, mannose, and arabinose, after sulfuric acid hydrolysis. Soluble lignin was determined from the steam condensates by UV spectrophotometry at 205 nm, using an adsorbtivity of 110 l g^{-1} cm^{-1}.[23]

Lignin and total carbohydrates of the solids were determined by sulfuric acid hydrolysis. A portion of the hydrolyzate was analyzed by GC for carbohydrates, after the addition of glucitol as an internal standard, by the method of Chen and McGinnis.[13] Another aliquot of liquid was neutralized with NaOH solution and analyzed for glucose on a YSI model 23A glucose analyzer. The insoluble lignin was collected in a tared glass filter crucible, dried, and weighed. One hundred ml of steam condensate was hydrolyzed with five ml of concentrated H_2SO_4 by refluxing for four hours and analyzing as above.

Acetone extraction of the air-dried pretreated solids was performed at room temperature by rinsing the solids in a glass filter crucible and analyzing the solids as above after calculating the amount extracted. Dilute alkali extraction (two percent NaOH refluxing for one hr), acid hydrolysis kinetics (20 percent H_2SO_4, 105°C, for six hours), and preparation of samples for electron microscopy have been previously described.[6]

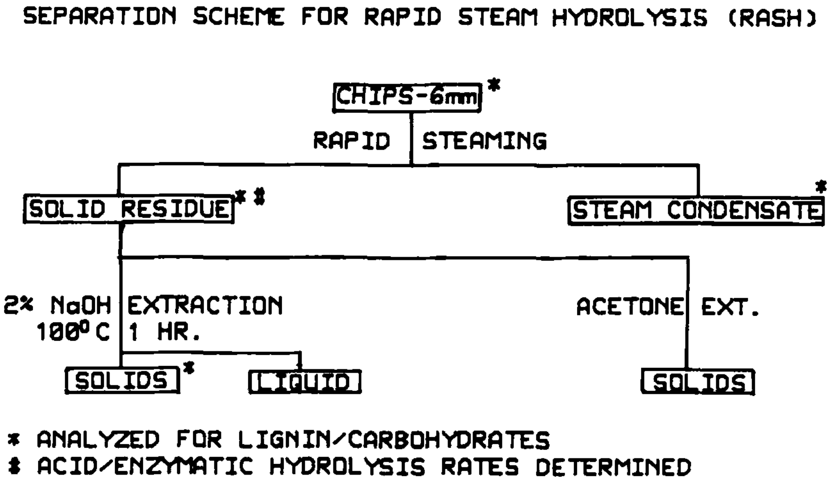

Figure 2. Separation scheme for rapid steam hydrolysis and product analysis.

Enzymatic hydrolysis was carried out with Meicelase brand cellulase (Meija Seika Kaisha, Japan) derived from *Trichoderma viride*. The enzyme solution consisted of 1.000 g cellulase per liter of 0.1 M sodium acetate buffered to a pH of 5.0 with 3.2 g of acetic acid, and 0.32 g of sodium azide as a preservative. To between 0.12 -0.14 g of solids pretreated by RASH, 10 ml of enzyme solution were added, and the mixture was incubated at 40.0°C in a shaker bath. At 6 and 24 hours, 20 μl samples were analyzed using the YSI glucose analyzer. Each run was standardized with filter paper (Whatman #1). A 120 mg Whatman No. 1 filter paper circle with 10 ml of enzyme solution gave 0.033 mg/ml/min of glucose, or 0.033 filter paper reducing sugar units after 1 hour. The reported values are based on the total available glucose in the solids.

Nitrobenzene oxidation was carried out at 160°C for three hours in a fluidized bed reactor. Ninety mg of lignin was added to 12 ml of 2 N NaOH and 0.8 ml of nitrobenzene. Thirty mg syringaldehyde and 20 mg of vanillin were used as controls. Continuous chloroform extraction of the reaction mixture was carried out for three hours and the chloroform discarded. The solution was then acidified and extracted for 20 hours with chloroform. The internal standard benzophenone was added to the chloroform, and the chloroform concentrated and acetylated with six ml of acetic anhydride, and 1/2 ml pyridine was added as a catalyst. Analysis was performed by GC using an OV-17 column.[14]

Infrared spectra of lignins were taken on a Perkin-Elmer model 257 infrared grating spectrophotometer. Lignin obtained by acidifying the base extraction liquid and lignin obtained directly from the steam condensate were compared to Klason lignin in KBr pellets.

Pyrolysis of lignin was carried out at 600°C for ten seconds in a CDS coil Pyroprobe interfaced to a GC equipped with an OV-17 column.

RESULTS AND DISCUSSION

The yield of solid material, based on the original ovendry weight, after pretreatment is shown in Figure 3. For a 1.0 minute steaming time, the wood chips begin to solubilize at 200°C while 50 percent of the weight is removed at 275°C. Most of the weight loss is due to removal of lignin and hemicellulose by the steam condensate.

Lignin appeared in the steam condensate at 210°C and above, as shown in Figure 4. More than half of the lignin appeared in the steam condensate at steaming temperatures of 275°C. The lignin must have been dissolved or at least suspended in the steam condensate and carried out of the reactor. About 20 percent of the lignin in the steam condensate from the 275°C run remained soluble after acid hydrolysis. The total amount of lignin increased slightly above 250°C. This was probably due to condensation of carbohydrate degradation products with lignin.

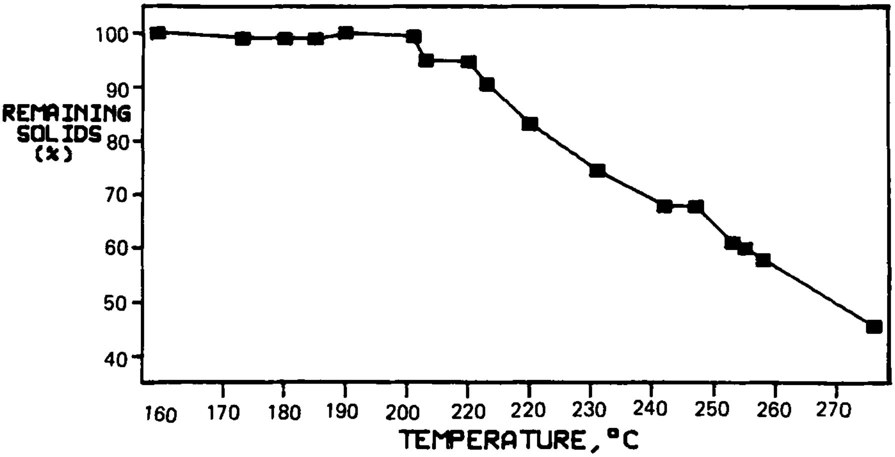

Figure 3. Percentage of material (based on original ovendry weight) remaining in the steaming reactor as a function of steaming temperature.

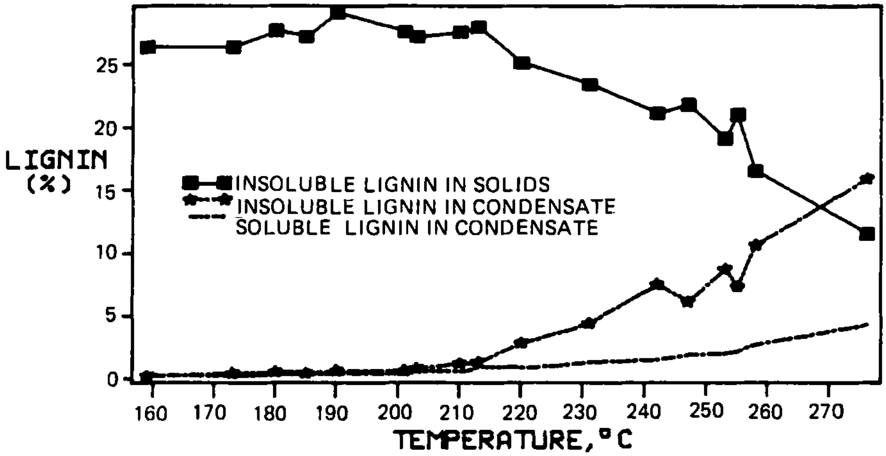

Figure 4. The percent of lignin in the pretreated solids and steam condensate as a function of steaming temperature, based on original ovendry weight of wood.

The hemicellulose fraction was monitored by measuring the free xylose and mannose that were obtained by acid hydrolysis of the various fractions. It is shown in Figure 5 that the hemicellulose appeared in the steam condensate at temperatures above 200°C. At the same temperature, the total amount of recovered xylose decreased due to decomposition of the xylose units themselves. Nevertheless, over 60 percent of the xylans appeared in the steam condensate at 240°C, over 20 percent remained in the solids, leaving less than 20 percent decomposition. This shows the abililty of rapid steam hydrolysis to fractionate hardwoods. Glucomannans (as mannose) accounted for about five percent of the material, and appeared to behave similarly to the xylans.

The cellulose fraction, on the other hand, remained in the RASH reactor with less than 20 percent decomposition even at 275°C. The remaining solids were enriched in cellulose as the lignin and hemicellulose were removed. Above 260°C, the solids

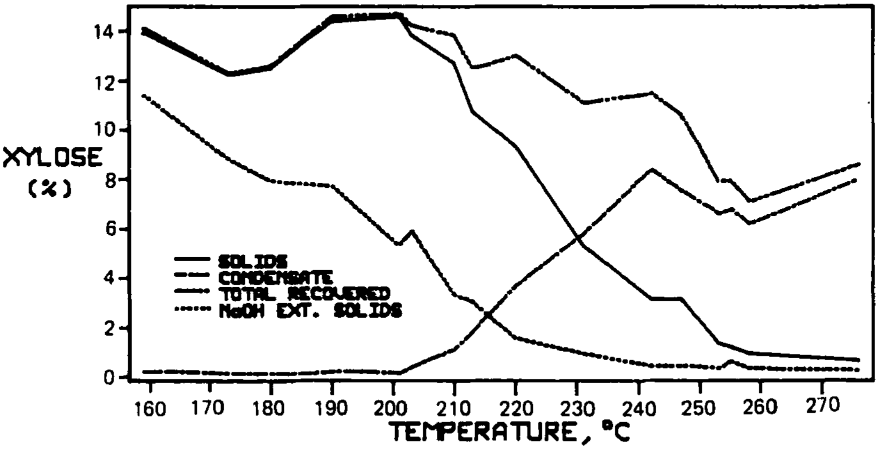

Figure 5. The occurrence of xylans (as xylose) in both steamed wood chips, the steam condensate the total xylans recovered, and xylans in alkali-extracted steamed solids.

contained over 70 percent cellulose, as monitored by glucose after acid hydrolysis. Schultz et al.[6] noticed some decomposition of cellulose when wood chips were steam exploded from 220-240° for one minute. Decomposition did not occur until much higher temperatures using RASH as a pretreatment. The explanation probably lies in the formation of acetic acid. Autohydrolysis of wood occurs as acetyl groups of the hemicelluloses are hydrolyzed at elevated temperatures in the presence of water to give acetic acid, lowering the pH to 3-4, which permits hydrolysis of the hemicelluloses.[15] Furthermore, secondary reactions are possible, depending on the concentration of acid and the temperature, such as the production of furfural (from the pentoses) and hydroxymethylfurfural (from the hexoses), which may be further converted to levulinic acid.[16] The removal of acetic acid in the RASH process reduces the amount of decomposition. To verify that acetic acid would degrade cellulose, a run with 4.5 percent acetic acid in the steam at 260°C degraded over 20 percent the cellulose.

Alkali extraction of the solids removed low molecular weight lignin and hemicellulose fragments. Surprisingly, as shown in Figure 6, over 30 percent of the cellulose could be removed from the solids of wood chips pretreated at the higher temperatures. Alkali extraction of the xylans proceeded at much lower temperatures of pretreatment. This is to be expected since xylans and mannans are more easily hydrolyzed and are much smaller molecules than cellulose. Even though no xylans were observed in the steam condensate at pretreatment temperatures of 200°C, over 50 percent of the xylans were removed by dilute alkali extraction. Casebier et al.[17] studied removal of xylans in southern yellow pine chips during autohydrolysis from 100-180°C for up to two hours. Their work indicated that xylans up to a molecular weight of 3100 could diffuse through the cell wall. Thus rapid steaming at temperatures below 200°C may partially hydrolyze the xylans; they may not appear in the steam condensate simply because they do not have time to diffuse through the cell wall.

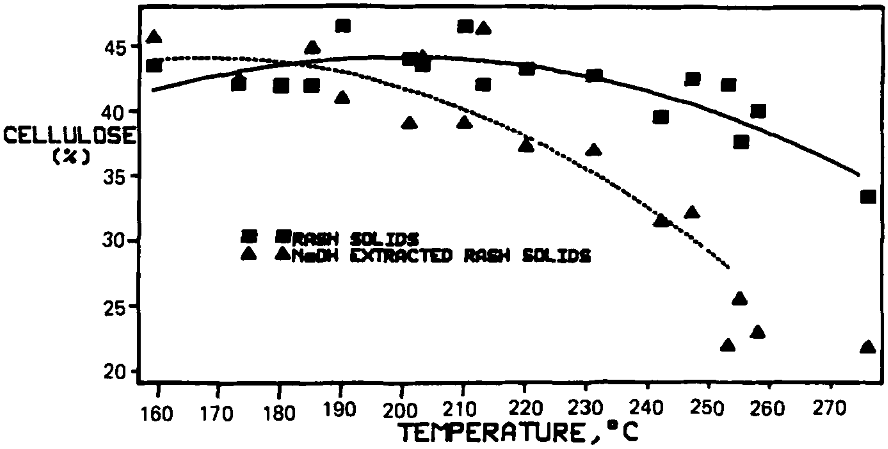

Figure 6. Cellulose remaining in the steamed solids both before and after alkali extraction.

As shown in Figure 7, alkali extraction of solids removed a constant amount of lignin. Acetone extraction of the solids at ambient temperature removed about ten percent of the lignin present in the original wood without removing much carbohydrate material, as the carbohydrates are not soluble in acetone.

The results of the acid and enzymatic hydrolysis of the steamed solids are shown in Table 1. The percent yields here are based on the total available glucose present in the solids. The rate of acid hydrolysis actually decreased slightly for the solid material which was steamed above 250°C. This suggests that there was no decrease in the crystallinity of cellulose during rapid steaming. Consequently, the rate of acid hydrolysis is not greatly affected. Marchessault, et al.[18] did not detect a loss in crystallinity of aspen chips which were steam exploded. On the other hand, the rate of enzymatic hydrolysis was greatly enhanced, probably due to disruption of the lignin network. Wood chips steamed at 250°C or above are hydrolyzed at a rate similar to that

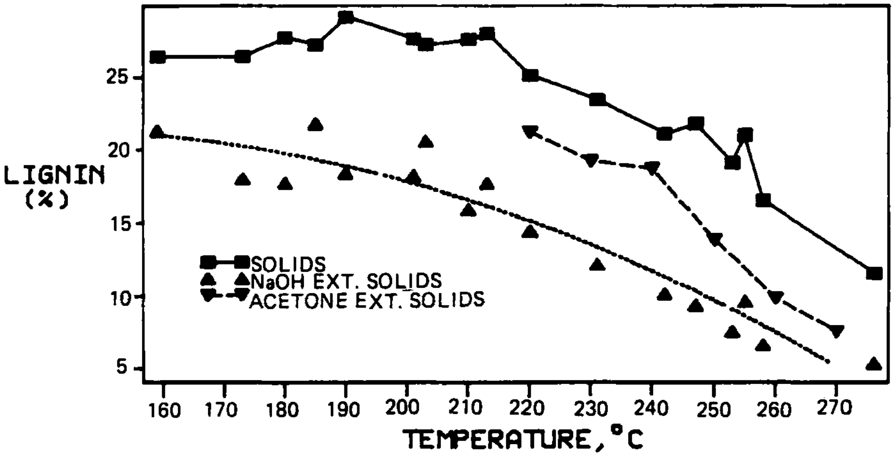

Figure 7. Lignin content of the steamed solids, after acetone extraction, and after alkali extraction.

TABLE 1

Enzymatic and Acid Hydrolysis of RASH Solids

Temperature, °C	6 hours	24 hours	Acid Hydrolysis
Control	2.6	4.0	17.0
220	5.6	10.7	16.4
230	6.4	16.0	17.1
240	7.7	18.5	16.8
250	8.2	21.5	14.0
260	12.8	24.0	14.2
270	13.3	23.6	14.8
Filter Paper	10.0	26.0	--

All figure are percent glucose hydrolyzed based on the total glucose content.

of filter paper. The enhanced rate of enzymatic hydrolysis in the case of steam explosion with aspen has previously been shown.[7,18]

The removal of polymer fragments through the steam condensate, the relatively short reaction times, and the removal of acids by the steam condensate, suggested that the lignin obtained by RASH should be especially reactive. We have done some preliminary experiments on a few of the lignins obtained. In rapid steaming, as in steam explosion, the lignin is softened due to its thermoplastic nature.[19] Electron microscopy of the steamed solids (Figure 8) shows a tendency for fiber separation at the compound middle lamella, which is highly concentrated in lignin. However, there is no physical action, with the RASH process such as that which occurs in steam explosion which allow defibration to occur on a large scale. At higher temperatures, beads form on the fibers. The beads are probably largely composed of lignin (8b), since dioxane-water extraction removes the beads.

Lignin which precipitates after neutralization of the two percent NaOH solution after base extraction of the 220°C steamed solids and lignin which precipitated directly from the steam condensate of a 275°C steaming run were compared to lignin in untreated wood by nitrobenzene oxidation and pyrolysis (Table 2). Carbohydrate analysis of the condensate lignin showed less than two percent carbohydrates; also, this lignin was soluble in acetone. The condensate lignin (275°C) appears about as reactive as HCl lignin, and the alkali-extracted lignin (220°C) was almost as reactive as the native lignin. The yields from the pyrolysis were higher than Klason and HCl lignin from mixed hardwoods.[20] These results are being confirmed by additional studies.

The Infrared spectra of some lignins were obtained. The Klason lignin lacks peaks characteristic of uncondensed guiaicyl units (1035 and 1270 cm^{-1}),[21,22] while these peaks were apparent in the RASH lignins. The RASH lignins also exhibit absorption due to carbonyl groups.

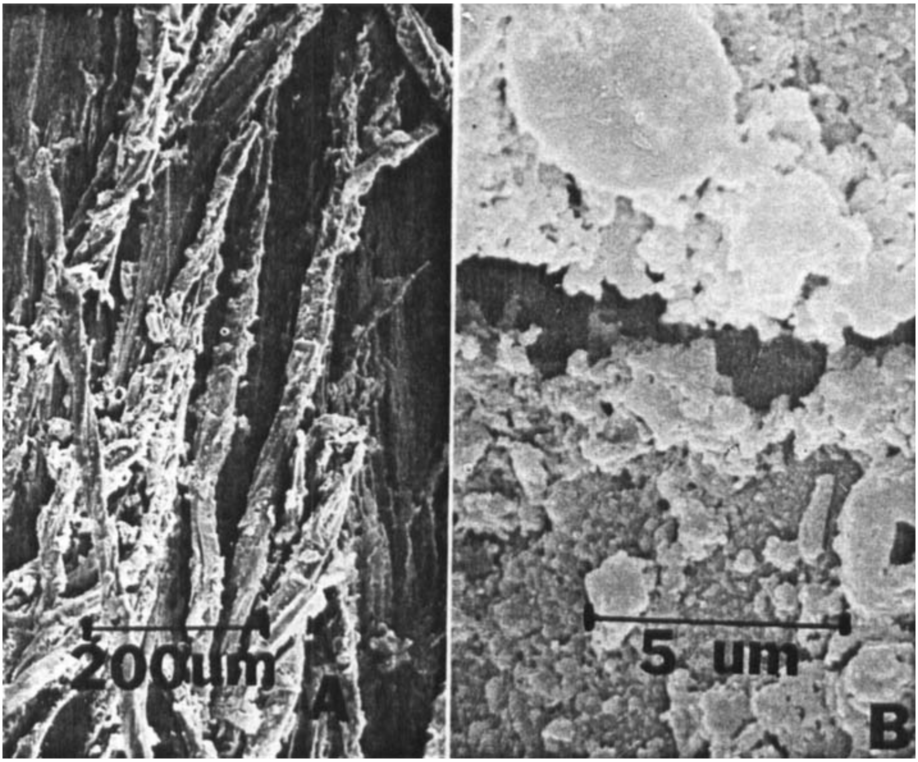

Figure 8. Scanning electron micrograph showing some defibration of wood fibers in "A" and the rough surface of the fibers believed to be caused by lignin in "B".

TABLE 2

Product Yield from Nitrobenzene Oxidation and Pyrolysis of Lignin

Sample	Nitrobenzene Oxidation Yield, Weight %		Pyrolysis Yield, Weight %	
	Vanillin	Syringaldehyde	Guaiacol & Methylguaicol	Syringaldehyde & Methylsyringyl
Control-Mixed Hardwood Chips	11.9	18.3	--	--
Alkali: Ext. Lignin 220°C	5.5	17.6	0.67	1.89
Condensate Lignin 275°C	4.0	9.3	0.77	1.42
HCL (Mixed Hardwood) Lignin	5.4	14.3	0.41	1.25
Klason (Mixed Hard-wood) Lignin	0.1	0.3	0.12	0.19

CONCLUSIONS

Rapid steaming of hardwood chips with continuous removal of steam condensate and products is similar to steam explosion with some important differences. Since there is no explosion at the end of the process, rapid steaming of wood chips could be set up as a continuous process. Rapid steam hydrolysis is able to fractionate wood, leaving a cellulose-rich fraction in the steaming reactor. Partible products can be removed with the steam condensate before extensive secondary reactions occur; consequently, degradation of separated components can be kept to a minimum. Removal of acetic acid and other acids formed during steaming probably account for the increased stability of cellulose in steaming compared to steam explosion under similar conditions. Removal of the acids may also prevent condensation reactions of lignin. One disadvantage of rapid steaming is that the chips are not defibrated as they are in steam explosion.

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