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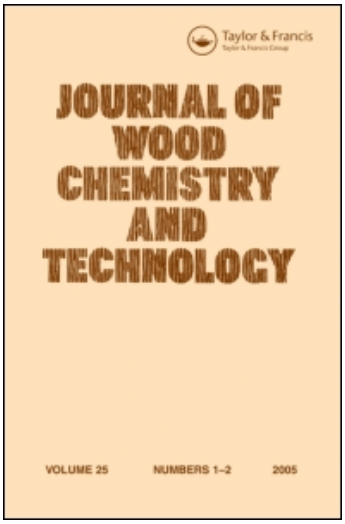

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EFFECT OF SULPHUR DIOXIDE AND SULPHURIC ACID ON STEAM EXPLOSION OF ASPENWOOD

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ABSTRACT

The use of steam explosion as a pretreatment for woody biomass prior to enzymatic hydrolysis has been proposed in the past. In this study the effect of SO_2 impregnation (1.6% SO_2 on dry wood input) and H_2SO_4 impregnation (0.58% H_2SO_4 on dry wood input) on the exploded substrates produced are compared with the case where no acid was added. Both acid catalysts substantially improve the survival of pentose sugars when treatments of equal severity are compared. H_2SO_4 however reduces the extent to which lignin may be extracted from the water washed exploded substrates with caustic.

The mode of action of the SO_2 has been examined and, at the levels used in this work, approximately 50% of the input sulphur is shown to bind to the substrate forming, most likely, lignosulphonates.

The enzymic digestibilities of the acid impregnated steam exploded substrates are compared with those of the non-acid impregnated material and are shown to be more easily saccharified.

INTRODUCTION

Steam explosion of lignocellulosics such as agricultural and wood residues has received considerable attention in the past as

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a pretreatment for the enzymatic hydrolysis of such substrates for fermentation by a variety of organisms. The process has the potential of being a cost effective pretreatment in the biological conversion of lignocellulosic carbohydrates to chemicals and fuels.

The main limitations of steam explosion as a pretreatment for the utilization of aspenwood, carried out without added acid catalysts and under conditions which optimize the susceptibility of the treated substrate to enzymatic digestion, are that approximately 50% of the xylan in the wood is destroyed during the pretreatment, that the disruption of the lignin-carbohydrate matrix is incomplete and that compounds which are inhibitory to microorganisms used in downstream processing are generated as a result of lignin and carbohydrate degradation. Despite these limitations however, steam explosion appears to be the most promising commercial pretreatment option.

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Millet et al[1] have examined the use of SO_2 for enhancing the enzymatic degradation of cellulosic substrates and have shown that, with gaseous SO_2 at 120°C and 0.21 MPa (30 p.s.i.) for periods of 2-3h, sulphonation and substantial depolymerization of the lignin occur with a resulting disruption of the lignocellulosic complex. Essentially quantitative enzymic conversion of aspenwood carbohydrates to reducing sugars was then obtainable. The long reaction times involved in this pretreatment, and the high levels of SO_2 required, have prevented further development of this method.

The use of SO_2 as an acid catalyst during steam explosion of poplar has been reported[2] to improve the substrate enzymic susceptibility relative to that of material produced without SO_2 addition. Due to poor analytical procedures and no quantification of the SO_2 levels used, the General Electric report does not however allow a detailed examination of the chemical effects of the SO_2 addition to be made. The beneficial effect of SO_2 addition nevertheless was clearly demonstrated and gave nearly double the level of soluble sugars of the steam-only pretreatment on subsequent enzymic saccharification. The addition of

SO_2 during explosion pretreatment of the softwood Pinus radiata has recently been reported[3] to result in enhanced enzymic digestibility relative to that obtained without SO_2.

The impregnation of aspenwood with H_2SO_4 prior to steam explosion has been reported[4,5] and is known to improve sugar recovery following treatment and to enhance enzymatic digestion of the water washed pretreated substrate. Partial acid hydrolysis at 160 to 220°C of 70-mesh oakwood, as a 5% slurry in a continuous plug-flow reactor, has also been shown[6] to greatly enhance subsequent enzymatic hydrolysis.

The work reported here details the effects of SO_2 (added to aspenwood prior to steam explosion) on the survival of carbohydrates in the process, on the extractability of the hemicellulose and lignin fractions in the exploded substrates and on the enzymatic digestibility of the unwashed and water washed pretreated materials. These results are compared with those obtained with aspenwood which had received no SO_2 treatment and aspenwood that had been impregnated with dilute (0.2%) H_2SO_4.

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EXPERIMENTAL

Wood Supply

Aspen (Populus tremuloides) logs were chipped in the green condition to give chips 3.2 mm in the fibre direction. These chips were then screened and only the fraction passing through the 25 mm screen and retained by the 6.2 mm screen (89.2% of all chips) was kept for experimental use. The chips were stored at -4°C until required.

Acid Impregnation

H_2SO_4 impregnation was performed by vacuum impregnating green chips with a large excess of 0.20% H_2SO_4 at room temperature for 60 hours. During this period the acid was drained and replaced with fresh acid several times. The chips were finally blotted

dry using paper towels and stored at $-4^{o}C$ until needed. These chips had a dry-matter content of 36.27% and analysis of the chip material for total sulphur gave a value of 0.19% (O.D. basis), which is equivalent to 0.58% H_2SO_4 (O.D. basis).

SO_2 impregnation was achieved by passing anhydrous SO_2 gas into a plastic bag containing green chips (48.03% dry-matter content). The uptake of SO_2 was measured by weighing the bag of chips before and after SO_2 addition and is expressed as a percentage of the ovendry (OD) wood. The uptake was very rapid and by observation of the chip colour appeared to be uniform. SO_2 impregnated chips were prepared in portions of 200 g equivalent dry weight and were used within 0.5-1.0 hour of SO_2 addition. The chips were added directly to the steam explosion gun from the plastic bag.

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Steam Explosion Gun Operation

A 2 litre gun constructed of 316 stainless steel was used throughout this work. The gun barrel (63 mm inside diameter) is fitted with a 75 mm rapid opening air actuated ball valve at the lower end and a Parr Instrument Company bomb lid at the top. The lid carries a pressure gauge, a bleed valve and thermocouple probes. Saturated steam at temperatures adjustable up to $250^{o}C$ enters the gun near the top of the gun barrel. When the lower ball valve is opened the wood mass and steam is violently discharged through a curved pipe into a receiving cyclone (approx. 50 litres) at atmospheric pressure that allows quantitative recovery of liquid and solid products.

Typical operation of the unit involves preheating the well insulated assembly to the desired temperature by repeatedly filling and firing with steam only. The Parr lid is then rapidly removed (10 seconds) and the wood material shaken in from a plastic bag. The lid is then replaced (10-15 seconds) and steam introduced immediately. As indicated by the thermocouple located in the Parr lid the steam temperature within the

wood chip bed reaches the set boiler temperature within 6 seconds, and in all cases treatment times reported here are additional to this 6 s period. After the allotted time the lower ball valve is pneumatically opened and the contents of the cyclone are recovered. Material held up in the gun assembly is negligible.

Washing of Steam Exploded Substrate

Water washing of steam-exploded aspenwood (SEA) was carried out using an overhead pneumatic stirrer at a consistency of 5% (dry basis). After an initial wash for 1 hour the solids were removed by filtration on a 70 μm expanded polyethylene filter and then again stirred for 0.5 h with the same volume of fresh distilled water. Filtration then gave the water insoluble fraction (SEA-WI) of the steam exploded aspenwood and the water soluble solids (SEA-WS) in the combined filtrates.

Where necessary NaOH washing of the SEA-WI was performed by stirring a 4% slurry of the substrate in 0.4% NaOH for 1 h. The NaOH solution was filtered off and the solid residue washed, first with small portions of 0.4% NaOH, and then with distilled water to neutrality. Lignin in the NaOH extract was precipitated by the addition of H_2SO_4 and a small amount of chloroform[7].

Ethanol washing of SEA-WI was carried out at room temperature with an amount of ethanol calculated to give a final concentration of 90% v/v. The slurry (approx. 3% solids w/v) was stirred for 1 h, filtered and the solids washed with two further small portions of ethanol. The residue remaining upon removal of the ethanol/water from the extract was the ethanol soluble lignin reported.

Analytical Methods

Pentosan analyses were performed according to TAPPI standard T223-os-71. Klason lignin determinations were carried out as

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per TAPPI standard T222-os-75 and the acid soluble lignin in the filtrate from the Klason lignin analysis was measured by U.V. absorbance at 212 nm. A standard curve prepared using a fractionated sample of aspen milled wood lignin was used for the acid soluble lignin determination.

Total reducing sugars were estimated by the PAHBAH colorimetric method[8] and individual wood sugars were analysed by gas chromatography as their alditol acetates. A cold on-column capillary injector, with allose used as an internal standard, gave accurate quantitative results. Post hydrolysis of SEA-WS samples, in order to ensure all carbohydrates were in their monomeric state was carried out using refluxing 2M trifluoroacetic acid for 3 h.

Elemental sulphur analyses were performed by the Canada Centre for Mineral and Energy Technology (CANMET) using a high temperature combustion technique (ASTM method D4329).

The enzymic susceptibilities of various exploded wood fractions (SEA, SEA-WI, SEA-WS) were assessed using a combined enzymatic hydrolysis and fermentation (CHF) procedure[9]. Substrates were weighed and mixed with fermentation media in Wheaton serum bottles at 5% substrate concentration. Glacial acetic acid (adjusted to pH 6.5 with KOH) was added wherever necessary to bring the initial acetate concentration to 0.5% (w/v). Hydrolysis was initiated by the addition of sterile Trichoderma harzianum E58 culture filtrates - the final enzyme activities (xylanase or endoglucanase) were adjusted to 100 I.U. per ml of CMC'ase activity. Inoculation of the medium with Klebsiella pneumoniae cells (5% v/v) was carried out at the outset of the CHF process. The entire procedure was performed at 30°C, pH 6.5, with shaking at 150 r.p.m. and under finite air conditions. Xylan and Solka floc were run as control substrates. Sampling was carried out over a period of 4 days and the solvent figures reported are the highest of those obtained on days 3 or 4. 2,3-Butanediol and ethanol were analysed by gas chromatography.[10]

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TABLE 1

Analytical Data for SO_2 Impregnated, Steam Exploded Aspenwood (1.6% SO_2 based on O.D. wood, 120 seconds)

Steam Temperature (°C)	SEA				SEA-WI		
	Recovery [a] (% wood input)	Composition			Recovery (% SEA)	Composition	
		Pentosan [b] (% SEA)	Pentosan [b] (% wood input)	Apparent Lignin (% SEA)		Pentosan (% SEA-WI)	Lignin (% SEA-WI)
201	97.4	16.8	16.4	KL [c] 22.5 ASL [d] 3.1 TAL [e] 25.6	66.6	3.4	KL 28.3 ASL 2.6 TAL 30.9
210	92.1	15.9	14.6	KL 22.6 ASL 3.9 TAL 26.5	70.8	1.8	KL 29.3 ASL 1.9 TAL 31.2
220	90.3	14.3	12.9	KL 23.2 ASL 3.4 TAL 26.6	68.0	0.4	KL 30.8 ASL 2.7 TAL 33.5
227	86.0	13.2	11.4	KL 23.7 ASL 4.2 TAL 27.9	65.7	0.6	KL 32.7 ASL 2.2 TAL 34.9

SEA = steam exploded aspen SEA-WI = water insoluble material remaining after water washing of SEA

All figures on oven dry basis

[a] SEA recovered expressed as % O.D. wood input to gun

[b] pentosan content of original wood = 18.3%

[c] KL = Klason lignin

[d] ASL = acid soluble lignin

[e] TAL = total apparent lignin

RESULTS AND DISCUSSION

Effect of SO_2 on wood components

Aspenwood chips which had been impregnated with 1.6% SO_2 (based on O.D. wood) as described in the experimental section were treated in the steam explosion "gun" for 120 s at saturated steam temperatures ranging from 200-227°C. Analytical data for the various products obtained are presented in Table 1. The relatively low level of SO_2 impregnation was chosen so that chemical costs in any commercial application would be minimized. The treatment time of 120 seconds is considered to be in the "practical" range for steam explosion. For very short treatment times e.g. 20-40 s there is evidence[4] that for green wood chips uneven cooking can result. Such short treatments should therefore be avoided.

In the temperature range examined (Table 1) the survival of pentosan (in the form of both water-insoluble pentosan and water-soluble oligosaccharides and monomeric xylose) ranged from 89.6 to 62.2% of the original pentosan in the wood. Water washing of the SEA removed the bulk of the pentosan at all temperatures but by 220°C the residual pentosan in the water washed substrate was negligible. We consider that the optimum treatment temperature in this series is 210°C since over 90% of the pentosan in the SEA can be washed out with water (leaving 9% of the original pentosan in the SEA-WI) and the overall survival of pentosan (79.8%) is very high.

Water washing of the SO_2 impregnated SEA removed from 30 to 35% of the material. The wash liquor contained soluble hemicellulose sugars, solubilized lignin, wood extractives, acetic acid (derived from O-acetyl groups) and degradation products of these moieties (formic acid, furfural etc.). Under the more severe conditions a portion of the more resistant cellulose component of the SEA may have been solubilized. Following a

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TABLE 2

Carbohydrate Analysis of Water Soluble Material From SO_2 Impregnated Aspenwood[a]

	Steam Temperature			
	201°C	210°C	220°C	227°C
Total sugars[b] (% input wood)	16.3	17.2	17.9	19.3
Total sugars[b] (% SEA-WS)	52.6	56.0	56.8	61.1
Carbohydrate Composition (%)				
Arabinose	2.2	2.0	1.7	1.7
Xylose	75.1	69.7	58.2	46.7
Mannose	8.8	8.6	7.4	6.6
Galactose	3.1	2.8	2.4	2.2
Glucose	10.8	16.9	30.4	42.8
Xylose (% input wood)	12.2	12.0	10.4	9.0

All figures on oven dry basis
[a] See Table 1 for treatment details
[b] quantified via alditol acetate method, following post hydrolysis with trifluoroacetic acid

mild post hydrolysis of the aqueous wash liquor, in order to convert any polymeric carbohydrates to the monomeric state, analyses of the carbohydrates present in the wash liquors of the four products described in Table 1 were performed. The data are shown in Table 2. The soluble sugars account for 16.3 to 19.3% of the original wood but only between 52.6 and 61.1% of the solids in the SEA-WS. The balance of the solids in the SEA-WS comprises primarily 4-OMe-glucuronic acid (and small amounts of the acid resistant aldobiuronic acid from the xylan) which is not accounted for by the alditol acetate method, solubilized lignin and the original hot water extractives. Even

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under the mildest conditions used (201°C), where 12.4% of the original wood xylan remains in the SEA-WI, there is a significant quantity of hexose sugars solubilized. It appears that the solubilization of the aspenwood glucomannan, which is present as approximately 3% of the original wood[11], and of the small amount of wood galactan, occurs extremely rapidly and under the most mild conditions used here was essentially complete.

Comparison of effects of SO_2 and H_2SO_4 during steam treatment

In order to make a valid comparison of steam explosion carried out in the absence of acid with that following impregnation with H_2SO_4 or SO_2, it was decided to use the level of pentosan remaining in the steam exploded wood after water washing as a measure of the effectiveness of pentosan removal. With a view to solubilizing a large proportion of the wood xylan, but at the same time minimizing the destruction of pentose sugars, a level of 2% xylan in the SEA-WI was chosen.

Tables 3 & 4 list the analytical data for three "equivalent" substrates prepared so as to conform to this criterion. Accordingly the pentosan contents of the SEA-WI fractions of the three steam exploded products are very similar (1.3 to 2.1%). The different time and temperature conditions required to generate these substrates reflect primarily the acidity prevailing during the reaction. The data show very clearly that the survival of the pentose sugars is much greater for the acid (SO_2 and H_2SO_4) impregnated wood samples - values of 79.8% and 84.7% of the original pentosan in the wood for the SO_2 and H_2SO_4 respectively compared with 48.1% for the non-impregnated sample.

Recent work by Scott *et al*[12], and Springer and Harris[13], reported this effect. At about pH 4, the pH of unimpregnated aspenwood during steam treatment, the destruction of xylose by hydroxyl ions is appreciable. The very low hydroxyl ion concentration at this pH is sufficient to cause this effect

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TABLE 3

Analytical Data for Steam Exploded Substrates Prepared With and Without Acid Catalysts to Equal Degree of Pentosan Solubilisation and/or Destruction[a]

Treatment Conditions	SEA				SEA-WI		
	Recovery	Composition			Recovery	Composition	
		Pentosan		Apparent Lignin		Pentosan	Apparent Lignin
	(% of wood input)	(% SEA)	(% wood input)[b]	(% SEA)	(% SEA)	% SEA-WI	% SEA-WI
No added acid 120 seconds 240°C	89.9	9.8	8.8	KL 26.9 ASL 3.0 TAL 29.9	79.0	2.1	KL 30.3 ASL 1.8 TAL 32.1
1.6% SO_2 120 seconds 210°C	92.1	15.9	14.6	KL 22.6 ASL 3.2 TAL 25.8	70.8	1.3	KL 29.4 ASL 1.8 TAL 31.2
0.58% H_2SO_4 80 seconds 200°C	94.1	16.4	15.5	KL 22.4 ASL 2.6 TAL 25.0	70.5	2.0	KL 29.2 ASL 1.5 TAL 30.7

[a] All figures on an oven dry basis

[b] Pentosan content of original wood - 18.3%. Listed values of surviving pentosan represent 48.1, 79.8 and 84.7% respectively, of original pentosan

TABLE 4

Analytical Data for Water Soluble Material From Steam Exploded Substrates Prepared With and Without Acid Catalysts

	Treatment Conditions		
	No added acid 120 sec, 240°C	1.6% SO_2 120 sec, 210°C	0.58% H_2SO_4 80 sec, 200°C
Total sugars[a] (% input wood)	9.5	17.2	16.5
Total sugars[a] (% SEA-WS)	48.0	56.0	57.2
Carbohydrate Composition (%)			
Arabinose	2.7	2.0	1.9
Xylose	72.0	69.7	74.4
Mannose	9.5	8.6	8.8
Galactose	2.7	2.8	2.8
Glucose	13.0	16.9	12.0
Xylose (% input wood)	6.8	12.0	12.3
Apparent Lignin (% SEA-WS)	n.d.	KL 2.5 ASL 6.1 TAL 8.6	n.d.

[a] quantified via alditol acetate method, following post hydrolysis with trifluoroacetic acid

because it is a much more effective degradation catalyst than is the hydrogen ion. Figure 1 shows the two competing degradative pathways.

The degradation of xylose and xylan via hydroxyl ions is observed not only as a decrease in the yield of xylose but also as the production of material referred to as "pseudolignin"[4]. The high total apparent lignin of the non acid catalyzed sample (29.9%

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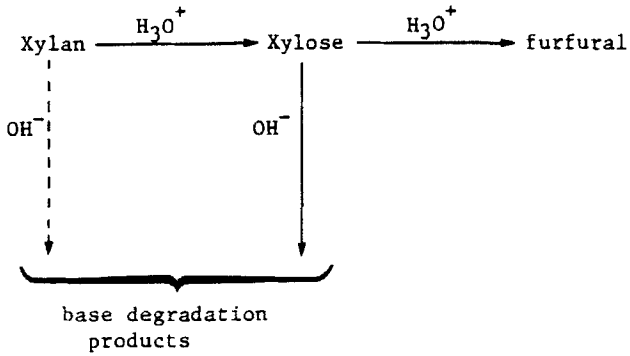

FIGURE 1: Degradation of Pentosan by Acid/Base Pathways

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of SEA) compared with that of the acid catalyzed samples (25.8% and 25.0% of SEA), as presented in Table 3, is due to pseudo-lignin being analyzed as Klason lignin. It is important to note that under the acidic conditions, the recovery of xylose plus furfural from xylan will be greater than 90% - furfural is easily recovered from steam condensate and is a valuable chemical.

The effectiveness of SO_2, as an added acid catalyst during autohydrolysis, has also been reported by Wayman[14] and the improved yields of fermentable sugars from both hardwoods and softwoods, was substantial when SO_2 (at 3% SO_2 based on dry wood) was added. In order to pretreat woods prior to hydrolysis in either plug flow or extrusion reactors, the SO_2/steam explosion option, giving high sugar recovery and physical disruption of the wood chip structure, is an attractive option.

The recovery or extraction of lignin from steam exploded substrates is of importance as it has been demonstrated that such lignin from non acid impregnated aspen is of low molecular weight and retains much of its original functionality. In order to examine the effect of the SO_2 and H_2SO_4 acid catalysts on lignin extractability the water washed SEA (SEA-WI) was extracted with

0.4% aqueous NaOH or 90% ethanol (both at room temperature). The results of these extractions are presented in Table 5. There is little difference between the SO_2 and non acid substrate in terms of the amount of lignin extractable with alkali (15.6 and 15.9% of original wood respectively). With the H_2SO_4 sample it appears that the lignin is somewhat more condensed during the explosion treatment as only 10.6% of the original wood was extracted from the SEA-WI. This difference is influenced to some extent by the mode of action of SO_2.

The amount of material extractable with 90% ethanol at room temperature is in all cases lower than for caustic. There is still however a large proportion (64.8% for non acid, 54.6% for SO_2 and 44.2% for H_2SO_4) of the lignin in the water washed substrate that is extracted into the ethanol. These figures would presumably rise with higher extraction temperatures. When comparing the effectiveness of ethanolysis[15] and steam pretreatment of aspenwood as a means of fractionating the wood into its component parts (viz lignin, hemicelluloses, cellulose) it should be borne in mind that not only the quantity and quality (activity) of the lignin is important but also the temperature and pressure regime for the extraction process must be considered. We have not examined the extracted lignin fractions in this study for molecular weight distribution or degree of condensation.

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Mode of Action of SO_2

In order to determine the mode of action of the SO_2 during the steam treatment a sulphur balance was carried out on the product under typical conditions. When compared with H_2SO_4, SO_2 may act as a weak acid by simply dissolving in the water in the green wood chips to form sulphurous acid, it may selectively attack the wood lignin to form lignosulphonates which are very strong acids, or it may act in both these ways depending upon the level of SO_2 impregnation.

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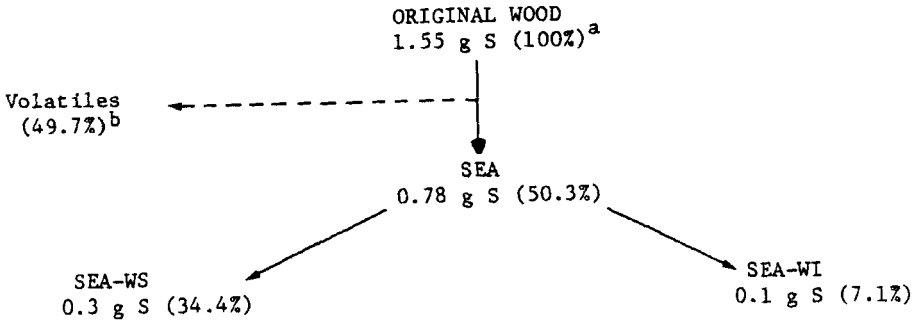
TABLE 5

Lignin Extractability of Non Acid and Acid Impregnated Aspen Steam Explosion Substrates

Treatment Conditions	Material Extracted by NaOH			Material Extracted by 90% Ethanol		
	% SEA-WI	% original wood	% apparent lignin[a] in SEA-WI	% SEA-WI	% original wood	% apparent lignin in SEA-WI
No Acid 120 seconds 240°C	26.6	15.9	82.9	20.8	12.5	64.8
1.6% SO_2 120 seconds 210°C	24.9	15.6	79.8	17.0	10.7	54.6
0.58% H_2SO_4 80 seconds 200°C	16.0	10.6	52.1	13.6	9.0	44.2

All figures on O.D. basis

[a] Extractable material expressed as a percentage of total apparent lignin in SEA-WI



[a] Sulphur expressed as % of input sulphur
[b] by difference

FIGURE 2. Sulphur Balance for Typical SO_2 Impregnated Wood Sample (based on 200 g O.D. wood input)

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The sulphur balance data are shown in Figure 2. Approximately 50% of the input SO_2 remains in the exploded substrate following explosive decompression and air drying at room temperature of the resulting exploded wood, indicating that at the level of SO_2 impregnation in this study (1.6% of O.D. wood input) half of the SO_2 is acting as sulphurous acid or is present in the vapour phase in the void volume of the gun. Water washing removes the large majority of the retained sulphur but, significantly, some 7% of the original sulphur remains in the washed substrate. The sulphur located in the water solubles is non volatile since freeze drying of the wash liquors did not result in a total loss of sulphur. Approximately one third of the total original sulphur remains in the dry water solubles. In addition, to cover the possibility that the water soluble sulphur was present as inorganic sulphite following reaction with the wood ash, a sample of the water solubles was passed through IR 120 (H^+) to remove any cations and was then freeze dried. The freeze dried solids from this sample gave the same sulphur level as that shown in Figure 2.

The mode of action of SO_2 in sulphite pulping is well established[16] and at high levels of SO_2 addition extensive depolymerization of hardwood lignin occurs at 120°C for 2h.[1] Although we have not isolated any lignosulphonates from the water soluble material in this work it is virtually assured that the sulphur is bound to lignin fragments rather than to any soluble or insoluble carbohydrate moiety.[17] These results are in contrast to the data presented by Mamers[3] who found no sulphur incorporation when treating Pinus radiata at SO_2 levels of 2-18% of wood input. The nature of the wood (hardwood versus softwood) and the level of SO_2 impregnation may account for this difference.

The total quantity of lignin found in the water soluble fractions for each of the three treatments examined is approximately 10% of the lignin in the original wood. It would seem that the SO_2 is not solubilizing the lignin to a significantly greater extent but, if the lignin is considered to be composed of phenyl propane units, then more than half of these soluble units must carry a sulphonate group.

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Enzyme Digestibility and Fermentability of Steam Exploded Substrates

A comparison of the effectiveness of the various process conditions (H_2SO_4, SO_2, no added acid) in pretreating the aspenwood was made on the basis of the quantity of solvents produced when using a combined enzymatic saccharification and fermentation (CHF) procedure.[9] This method assesses the enzymatic susceptibility of the substrates and the fermentability of the products of the saccharification, quantitative data being obtained by gas chromatographic analysis for 2,3-butanediol and ethanol.

Table 6 compares the solvent yields (2,3-butanediol and ethanol) obtained. Xylan, isolated from aspenwood in our laboratory[18], was the control substrate for SEA-WS substrates and Solka floc the control for SEA-WI substrates. At the 5% substrate level tested, the SEA obtained from acid (SO_2 or H_2SO_4) impregnated aspen is a substantially better substrate for CHF - giving solvent yields approximately three times as great under the test conditions. Similarly the water washed

TABLE 6

Production of 2,3-Butanediol and Ethanol from Various Fractions of Steam Exploded Aspenwood by the CHF Process[a]

Substrate[b] Fraction	Solvents[c] Yield (g/L)	Percent of[d] Theoretical	Solvents Yield[e] (g/100 g original wood)
SEA	2.2	11	4.0
H_2SO_4-SEA	7.2	35	12.4
SO_2-SEA	7.2	35	13.5
SEA-WI	5.2	28	7.3
H_2SO_4-SEA-WI	7.7	41	10.8
SO_2-SEA-WI	8.0	42	11.2
SEA-WS	0.9	6	0.6
H_2SO_4-SEA-WS	1.9	10	1.1
SO_2-SEA-WS	1.4	8	0.8
Xylan	14.4	51	-
Solka floc	13.3	48	-

[a] Combined hydrolysis fermentation (CHF) was carried out at pH 6.5 and 30°C for 3-5 days. Final enzyme levels were set at 100 IU/mL of CMC'ase activity

[b] All substrates at 5% (w/v) concentration

[c] Solvents yield is the sum of 2,3-butanediol and ethanol

[d] % theoretical conversion is based on the experimental solvent yields as a percentage of the total theoretical yields as calculated below:

$$\text{Theoretical yield of solvents from pentosans} = \text{g substrate} \times \text{pentosan content} \times \frac{150}{132} \times 0.5$$

$$\text{Theoretical yield of solvents from hexosans} = \text{g substrate} \times \text{hexosan content} \times \frac{180}{162} \times 0.5$$

[e] Calculated as solvent yield per gram substrate x fraction yield x 100

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products (SEA-WI) showed the same trend although it was somewhat less marked. Relative to the control substrates the extent of CHF lies between 73-87% of the control for the SO_2 and H_2SO_4 SEA-WI products.

Under the test conditions used the water soluble fractions (SEA-WS) were only utilized to a minor extent, solvent production being 6%, 10% and 8% of theoretical for SEA-WS, H_2SO_4-SEA-WS and SO_2-SEA-WS respectively. The inability of the T. harzianum-K. pneumoniae organisms to use these soluble substrates is due to the presence of inhibitory or toxic components being concentrated in these fractions. At the 2% substrate level this inhibition was not observed and the equivalent solvent production as percent of theoretical for the three substrates were in the same order, 24%, 36% and 52%. This shows that the water soluble material derived from the acid impregnated aspenwood, is somewhat less toxic to the test micro-organisms - an important point as the presence of lignosulphonates from the SO_2 impregnated samples might have been particularly potent inhibitors - but nevertheless the toxic components in the water soluble fraction remains a problem that should be addressed.

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CONCLUSIONS

The beneficial effects of acid impregnation prior to steam explosion of aspenwood are observed as a decrease in carbohydrate degradation and an increase in enzymatic susceptibility of the substrates produced i.e. a more effective pretreatment. The ease with which gaseous SO_2 can be added to the wood and the apparent even distribution of the gas make this an attractive proposition commercially. In contrast sulphuric acid impregnation is difficult[12], is a more corrosive chemical to handle and results in wetter wood substrates. As the water in the wood structure consumes a large proportion of the steam energy required in steam explosion saturated substrates are to be avoided.

Impregnation of aspenwood with SO_2 or H_2SO_4, and steam explosion of the impregnated wood under conditions that were

equally effective in removing pentosan on subsequent water washing, gave products of essentially equal enzymatic digestibility, in which equal fractions of the lignin were water-soluble. In both cases the major part of the lignin remained in the water-insoluble fraction after water washing. Extraction of the water-insoluble fraction with dilute alkali, or with ethanol, resulted in the removal of much more lignin from the SO_2- than from the H_2SO_4- derived material. Both the water-soluble and water-insoluble lignin from the SO_2-derived material contained bound SO_2, presumably as sulfonic acid groups. Although these sulfonic acid groups did not increase the amount of the water-soluble lignin, they may conceivably have contributed to the alcohol- and especially to the alkali-solubility. Whether this greater solubility resulted from the presence of these groups, or from a lower molecular weight of the lignin, cannot be concluded without further work.

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