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Chemical cellulose from *Eucalyptus Regnans* wood by autohydrolysis–explosion–extraction

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Eucalyptus regnans woodchips and sawdust, which were autohydrolysed at 200°C and exploded at 6·9 MPa nitrogen pressure in the Siropulper pilot plant, gave pulp yields of 68–76% with pentosan contents of 0·9–2·0%, similar to those of pulps which were not exploded. Sodium hydroxide was the most effective medium tested for extraction of lignin from the pulps, and gave pulps with kappa numbers 35–45 after extraction at 100°C with 0·33 M NaOH. At 20°C, the extraction efficacy decreased in the order 0·125 M NaOH > 50% NH_3 > 0·2% $Ca(OH)_2$. For organic solvent extractions at 60°C, the order of extraction was 70% ethanol > acetone > ethanol. The viscosities of the *E. regnans* cellulose samples after autohydrolysis at 200°C for 5 min and extraction were higher than those of a commercial viscose-grade cellulose, and were progressively lower for samples autohydrolysed for longer periods. However, the polydispersities of the celluloses were higher, and the α-cellulose values were lower, than the commercial cellulose. The *E. regnans* wood gave acetate-grade cellulose by conventional prehydrolysis-alkali pulping procedures.

INTRODUCTION

Autohydrolysis of lignocellulosic materials such as wood or agricultural residues by application of steam at temperatures typically between 200 and 250°C, followed by explosive release of pressure, has been widely studied as a means of pretreatment of the lignocellulose before enzymic hydrolysis (Schultz *et al.*, 1989) or to increase the digestibility of feeds for ruminant animals (Brown & Bender, 1980). The pressures used for the explosive release of the digester contents may be that of the steam alone, as exemplified by the Iotech (De Long, 1979) and Stake (Muzzy *et al.*, 1983) technologies, or that obtained by application of an introduced gas as in the Siropulper plant (Mamers *et al.*, 1979). Although the efficacy of autohydrolysis-explosion for pretreatment of lignocellulose before its further conversion to low molecular weight chemicals has been conclusively demonstrated, the economics of the conversions have not yet been sufficiently attractive to lead to implementation of the technology.

Most of the lignin in autohydrolysed-exploded pulps may be extracted with organic solvents or with alkali, which provides a means of fractionating the polymers that comprise lignocellulose (Marchessault & St-Pierre, 1980; Overend & Chornet, 1987). The possibility of using the cellulose fraction for polymer applications rather than for low molecular weight products has received only minor attention. Bungay *et al.* (1983) have reported that cellulose obtained by alkali extraction of steam-exploded wood from an Iotech reactor had a degree of polymerisation (DP) too low for conversion to useful derivatives such as cellulose ethers. Steam exploding *Populus tremula* wood at 220–250°C for 15–165 s gave, after washing with water and extraction with aqueous dioxane, cellulose samples with DPs which decreased as the reaction times increased (Excoffier *et al.*, 1987; Barnet *et al.*, 1989). Other workers have demonstrated that the DP of cellulose is lowered after steam treatment of wood (Puls *et al.*, 1983; Körner *et al.*, 1984; Overend & Chornet, 1989) and of cellulose preparations (Yamashiki *et al.*, 1990*a*,*b*).

Unlike other explosion digesters, the Siropulper uses an applied pressure for the explosive release of digester contents, permitting lower autohydrolysis temperatures as high pressure steam is not required for the explosion. The lower reaction temperatures afforded in the

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Siropulper may allow the preparation of higher DP celluloses. The authors' preliminary study (Wallis & Wearne, 1985) showed that the viscosities of pulps obtained from autohydrolysis–explosion–extraction of various hardwoods were progressively lowered as the autohydrolysis time increased.

The world's annual capacity for chemical cellulose production from wood is 5·5 Mt (Hiett, 1985). Two processes are used to obtain the chemical cellulose, sulphite and prehydrolysis-kraft, the latter process permitting the manufacture of high purity, high DP cellulose (Hinck *et al.*, 1985). The present study was undertaken to assess whether the Siropulper explosion technology could provide an alternative route to commercial-grade chemical cellulose. To this end, chemical celluloses were prepared from *Eucalyptus regnans* wood by autohydrolysis–explosion–extraction processes, and their properties were compared with those of conventional alkaline pulps and prehydrolysis-alkaline pulps.

MATERIALS AND METHODS

Wood and cellulose samples

The *Eucalyptus regnans* sawdust was fresh material taken from a sawmill in the Melbourne area. The age of the trees processed ranged from 30 to 50 years.

The *E. regnans* woodchips were from a 12-year-old tree grown in the Toolangi district, Victoria. Cross-sectional discs of the logs were reduced to chips (25 × 20 × 3 mm) in a laboratory chipper.

Avicel PH-101, a microcrystalline hydrolysed cellulose, was obtained from FMC Corp, Melbourne. Two prehydrolysis-kraft hardwood cellulose samples, Acetakraft and Viscokraft, were obtained from International Pulp Sales Company, New York.

Analytical methods

Kappa numbers of the pulps were obtained by Australian Standard AS1301.201m-86.

Klason lignin contents of the pulp samples were determined by Australian Standard AS1301.11s-78. Acid-soluble lignins were obtained by the method of Bland and Menshun (1971), using the specific absorption coefficient of 100 g^{-1} litre cm^{-1} for the lignin.

α-Cellulose values were measured by TAPPI official method T203 om-88.

Carbohydrate analyses were carried out by a modified alditol acetate procedure as described by Wallis and Wearne (1985).

The pentosan contents of the celluloses were obtained by TAPPI classical method T223 cm-84.

The cuene viscosities were determined for 0·5% cupriethylenediamine solutions by TAPPI official method T230 om-82.

Autohydrolysis–explosion pulping

Air-dried *E. regnans* sawdust or woodchips (800 g o.d. (oven dry)) were placed in the Siropulper explosion digester (6-litre capacity). Heating was accomplished by a combination of direct steam injection and an electrical heating coil, and the autohydrolysis temperature of 200 °C was reached in 3–4 min. The steam valve was closed and compressed nitrogen was introduced to bring the digester to 6·9 MPa pressure. After the desired period at 200 °C, the digester contents were explosively discharged through an eight-bar nozzle into a collecting tank by actuating a valve. The pulp was filtered, washed with water, and screened in a 0·25-mm slotted Packer screen.

Additional autohydrolysis treatments at 200 °C for 5 and 20 min were carried out on the *E. regnans* woodchips without subsequent explosive release of pressure. The treated samples were disintegrated to pulps with a British Standard Disintegrator.

The pH of the aqueous liquor obtained after the autohydrolysis treatment was 3·1.

Alkaline pulping

Air-dried *E. regnans* sawdust or woodchip samples (300 g o.d.) and appropriate liquors were placed in 3-litre steel digesters, which were rotated in a heated air bath for the allotted time. The digesters were cooled, and the samples were disintegrated, washed with water, and screened in a 0·25-mm slotted Packer screen before pressing and crumbling.

Extraction of exploded pulps

For the alkaline extractions, wet pulps were used, but for the organic solvent extractions, the pulps were first air-dried. The pulps were placed in Erlenmeyer flasks with various solvents, and kept at the desired reaction temperature by immersion in a thermostatted water bath. For alkaline extractions at 100 °C, 3-litre steel pressure vessels heated in an air bath were used. After extraction, the pulps were washed well with water.

Lignin was recovered from the alkaline extraction liquors by dropwise addition of the extracts into a rapidly-stirred mixture of 0·5 M sulphuric acid and chloroform in the ratio 3 : 1 v/v. The volume of acid used was sufficient to retain acidity in the final solution. The lignin was collected on a sintered glass funnel and washed with water until the washings were neutral.

Lignin was isolated from the organic solvent extracts by concentration of the solvent in a rotary evaporator until lignin began to precipitate, addition of water to the concentrated extract, and finally freeze-drying.

Chlorite delignification of pulps

The procedure of Stone and Clayton (1960) was employed. A solution of sodium chlorite (20 g), anhydrous sodium acetate (20 g) and acetic acid (40 ml) was made up to 1 litre with water. The moist unbleached pulp at 20% stock concentration was mixed with sufficient chlorite solution to give a 5% stock concentration, and was allowed to react with occasional mixing for 24 h. After removal of the spent chlorite liquor, the pulp was washed with water. The chlorited pulps had a total lignin content of 2–4%, depending on the lignin content of the non-delignified pulp.

Sequential bleaching of alkaline pulps with hypochlorite-chlorine dioxide

Hypochlorite (H) bleaching of the kraft, soda and soda-AQ pulps was carried out in a polyethylene bag for 2 h at 40 °C at 10% stock concentration, using NaOCl and NaOH charges of 1·0 and 0·5% respectively (o.d. pulp basis). The treated pulps were washed with water.

The chlorine dioxide (D) stage followed the H stage, and was performed at 70 °C for 4 h and at 6% stock concentration. Chemical charges were for ClO_2, 0·5%; and for NaOH, 0·25% (o.d. pulp basis).

Molecular weight distribution of cellulose samples by high performance size exclusion chromatography of tricarbanilate derivatives

The molecular weight distribution of the cellulose samples was determined on their tricarbanilates by high performance size exclusion chromatography (HPSEC) in tetrahydrofuran according to the procedure of Evans *et al.* (1989). The tricarbanilates were prepared by reaction of the celluloses with phenylisocyanate in dimethylsulfoxide at 70 °C or pyridine at 80 °C. The HPSEC data were automatically acquired from the detector signal and were processed by application of DAOS/PC software (Laboratory Software Associates, Melbourne) on an Olivetti M-24 microcomputer. The weight average and number average degree of polymerisation ($\bar{P}_w$ and $\bar{P}_n$ respectively) values were obtained by use of appropriate computer software.

RESULTS AND DISCUSSION

Studies with *E. regnans* sawdust

Sawmilling residues such as sawdust and off-cuts are an important lignocellulose waste material, with 3 million tonnes being generated annually on a dry weight basis in Australia (Stewart *et al.*, 1979). Initial experiments were carried out with *E. regnans* sawdust from a commercial sawmill. All autohydrolysis experiments before explosive defibration in the Siropulper pilot plant were performed at 200 °C, as the authors' earlier study (Wallis & Wearne, 1985) showed that *E. regnans* woodchips could not be discharged from the Siropulper pilot plant after treatment at 170 °C for 20 min, and explosive release from 13·8 MPa nitrogen pressure. Autohydrolysed–exploded pulps were prepared by treatment of the sawdust for 5 min at 200 °C, and explosive release of the digester contents at 6·9 MPa pressure. These pulps have previously been shown to be very susceptible to enzymic saccharification with Trichodermal cellulase preparations (Dekker *et al.*, 1987).

Characteristics of the exploded pulp are given in Table 1. The pulp yield, 68·9% including 8·9% screen rejects, was typical for these pulps (Wallis & Wearne, 1985), and the lignin and xylan contents indicate that the former was essentially retained in the pulp, whilst the hemicelluloses were largely removed by the autohydrolysis. The cuene viscosity of the chlorited pulp, 5·57 mPa s, is in the lower end of the range for commercial chemical cellulose preparations (Hinck *et al.*, 1985). Kraft and soda pulps prepared from the same sawdust sample and chlorite delignified had considerably higher cuene viscosities, 17·5 and 17·2 mPa s^{-1} respectively.

The exploded sawdust pulp was extracted with various alkalis and organic solvents to test their efficacies for lignin removal before final purification of the cellulose. Extraction with solutions of sodium hydroxide, 50% aqueous ammonia and calcium hydroxide for 24 h at 20 °C (Table 1) gave pulps with yields and lignin contents that decreased in the order of extractants $Ca(OH)_2 > NH_3 > NaOH$. However, the lignin contents were far in excess of those of a technically bleachable-grade pulp (*cf.* lignin contents of the kraft and soda pulps). Extraction with sodium hydroxide for 2 h at 70 °C gave a pulp with a similar yield and lignin content to that obtained after extraction at ambient temperature (Table 1). After chlorite delignification, the pulp had a similar viscosity to the unextracted pulp, which shows that the alkaline extraction does not cause substantial cellulose degradation. The higher glucan content of the extracted pulp reflects its lower lignin content. The α-cellulose content of the chlorited pulp was low, 87·6%, probably because of a large fraction of low molecular weight cellulose in the pulp. After extraction of the exploded sawdust at 100 °C for 6 h, the limit of non-pressurised aqueous extraction, the lignin content of the pulp decreased to that approaching a bleachable-grade pulp, as reflected by its Kappa number (35·8).

The exploded sawdust pulp was extracted with the

Table 1. Pulps from *E. regnans* sawdust[a]

Pulp	Autohydrolysed-exploded[b]										Kraft[c]	Soda[d]
Extraction liquor	—	NaOH 0·125 M	Aqu. NH_3 (50% w/w)	$Ca(OH)_2$ 0·2%	NaOH 0·21 M	NaOH 0·21 M	NaOH 0·21 M	Acetone	Ethanol	Ethanol 70% aqu.	—	—
Liquor : pulp		24 : 1	20 : 1	55 : 1	22 : 1	22 : 1	22 : 1	10 : 1	10 : 1	10 : 1		
Temperature (°C)		20	20	20	70	100	100	60	60	60		
Time (h)		24	24	24	2·0	2·0	6·0	2·0	2·0	2·0		
Pulp yield (%)	68·9[e]	75·5	78·0	80·5	74·0	57·5	47·2	83·2	87·1	80·9	49·1	50·9
Kappa number	153				94·0	49·6	35·8	84	110	70	11·1	20·9
Lignin												
Klason (%)	33·4	15·7	18·1	19·7	15·9	10·1	7·3				1·9	2·6
Acid sol. (%)	2·4	1·2	1·4	2·8	1·4	0·9	0·9				1·5	1·8
Total (%)	35·8	16·9	19·5	22·5	17·3	11·0	8·2				3·4	4·4
Carbohydrate												
Xylan (%)	0·9				0·6						16·8	17·2
Glucan (%)	62·1				77·9							
Cuene visc.[f] (mPa S)	5·57				5·59			5·15	5·16	5·21	17·5	17·2
α-Cellulose[f]					87·6			87·7	90·1	88·6		
Lignin recovered (%)					24·1			13·4	10·2	14·9		

[a] Yields and analyses on sample basis.
[b] Treated at 200°C for 5 min, exploded with 6·9 MPa nitrogen pressure.
[c] 15% active alkali (as Na_2O, o.d. wood basis), 25% sulphidity.
[d] 15% NaOH charge (o.d. wood basis).
[c, d] Liquor : wood 5 : 1, 1·5 h to 170°C, 1·5 h at 170°C.
[e] Includes 8·9% screen rejects.
[f] Based on chlorite-delignified pulp.

organic solvents acetone, ethanol and 70% aqueous ethanol for 2 h at 60 °C. The yields and Kappa numbers of the extracted pulps, and the amounts of lignin recovered, indicate that the efficacies of extraction decreased in the order NaOH ≫ 70% aqueous ethanol > acetone > ethanol (Table 1). The chlorited-extracted pulps had slightly lower cuene viscosities than the unextracted pulp, and the ethanol-extracted pulps had higher α-cellulose contents than the acetone-extracted pulp.

Studies with *E. regnans* woodchips

E. regnans woodchips were subjected to autohydrolysis at 200 °C for 5–20 min and were exploded at 6·9 MPa nitrogen pressure. For comparison, two samples were treated for 5 and 20 min without the subsequent explosive release of pressure. The pulp yields decreased slowly with time, and the yield was not significantly different for the pulps autohydrolysed for 20 min with and without explosion (Table 2). The lower yield for the unexploded pulp after 5 min at 200 °C is probably due to difficulties in controlling the temperature for the relatively short period.

The autohydrolysed pulps were extracted with 0·33 M sodium hydroxide at 100 °C for 2 h. The pulps which were autohydrolysed for longer periods had lower extracted yields and lower lignin and pentosan contents (Table 2). Thus there was a progressive loss of both lignin and carbohydrate material from extracted pulps autohydrolysed for increasing periods. Most pulp samples had Kappa numbers of ~40; values close to those considered feasible for technical bleaching. The viscosities of the chlorite-delignified extracted pulps decreased with increasing autohydrolysis time, and there were only slight differences in viscosities between pulps that had been subjected to explosive defibration and those without. These results show that the explosion step did not cause an additional depolymerisation of the cellulose. Brownell and coworkers (Brownell *et al.*, 1986; Brownell & Saddler, 1987) found that, compared to autohydrolysis without subsequent explosive defibration, explosion of autohydrolysed aspenwood did not increase the yield of water-soluble material nor that of sugars after enzymic hydrolysis.

A series of prehydrolysis-alkali pulps were prepared from the *E. regnans* woodchips (Table 3), and their properties were compared with those of the alkali-extracted pulps (Table 2). The prehydrolysis (autohydrolysis) conditions were 1·5 h at 170 °C, and the yield of pulp after this time (69·5%) was similar to those of the pulps treated for 5 min at 200 °C. The kraft, soda

Table 2. Effect of explosive defibration on autohydrolysed *E. regnans* woodchips

Pulp no.	Time at 200 °C (min)	Explosion pressure (MPa)	Pulp yield (%)[a]	Alkali-extracted pulp[b]				
				Yield (%)[a]	Pentosan (%)[c]	Lignin (%)[a]	Kappa no.	Cuene viscosity (mPa s)[d]
P1	5·0	—	71·5	36·4	1·4	2·8	36·8	5·65
P2	5·0	6·9	75·8	43·5	2·0	6·0	70·6	5·45
P3	10·0	6·9	70·5	34·8	1·0	2·7	42·7	3·65
P4	20·0	—	69·8	28·0	0·7	2·2	38·8	2·68
P5	20·0	6·9	68·3	29·1	0·9	2·0	37·5	2·78

[a] O.d. wood basis.
[b] 0·33 M Sodium hydroxide, 2 h at 100 °C, 15 : 1 liquor : pulp ratio.
[c] Sample basis.
[d] On chlorite-delignified pulps.

Table 3. Prehydrolysis-alkali pulping of *E. regnans* woodchips[a]

Treatment[b]	Pulp yield (%)	Kappa number	Cuene viscosity (mPa s)	HD-bleached pulp		
				Cuene viscosity (mPa s)	α-Cellulose (%)	Pentosan (%)
—	69·5	—	—	—	—	—
Kraft[c]	32·9	8·4	17·7	14·3	97·1	1·3
Soda-0·1% AQ	33·5	5·9	16·6	13·3	96·7	1·5
Soda-0·5% AQ	32·5	6·2	13·7	11·4	96·6	1·5
Soda	34·1	7·1	17·5	13·1	96·6	1·4

[a] All cooks 1·5 h to 170 °C, 1·5 h at 170°, 5 : 1 liquor : wood ratio, for both prehydrolysis and alkaline pulping.
[b] 13% Active alkali (as Na_2O).
[c] 25% Sulphidity.

and soda-AQ pulps prepared from the prehydrolysed chips had similar yields (32–34%) and Kappa numbers (6–8%). After bleaching with an HD sequence, the pulps had viscosities (11–14 mPa s^{-1}), α-cellulose (~97%) and pentosan (<1·5%) values typical of high-purity commercial cellulose preparations. The viscosities of the unbleached pulps were correspondingly higher than for the bleached pulps, and it is of interest that the soda-0·5% AQ pulp had a lower viscosity than the soda-0·1% AQ pulp. A possible reason for this is the known ability of AQ to oxidise aliphatic hydroxyl groups of cellulose under alkaline pulping conditions (Wallis & Wearne, 1987), leading to glucosidic bond cleavage in the cellulose. Thus prehydrolysis-alkali pulping gave celluloses with significantly greater DPs and purities than those of the celluloses obtained from autohydrolysis–explosion–extraction.

Data on some commercial celluloses are given in Table 4. Acetakraft and Viscokraft are manufactured from hardwoods as feedstocks for the cellulose acetate and viscose rayon industries, respectively, and Avicel is a microcrystalline acid-hydrolysed cellulose. The viscosity of Acetakraft was lower than those of the prehydrolysis-alkali pulps (Table 3), whereas that of Viscokraft was closer to the viscosities of the autohydrolysed-exploded samples from *E. regnans* (Tables 1 and 2). The low viscosity of Avicel (2·10 mPa s^{-1}) is indicative of severe hydrolytic degradation in its preparation. All three samples had low pentosan contents (<2%), typical of chemical cellulose preparations (Hinck *et al.*, 1985).

MWD studies of cellulose samples by HPSEC

The MWD of cellulose gives more information on its polymer properties than a single viscosity measurement, and a preferred method for determining the MWD of cellulose is by HPSEC of its tricarbanilate derivative (Evans *et al.*, 1989). Data on the MWD of the commercial cellulose samples and the autohydrolysed-extracted pulps from *E. regnans* are given in Table 5, and Figs 1 and 2.

The three commercial celluloses have molecular weight characteristics in the order of decreasing molecular weight Acetakraft > Viscokraft > Avicel (Table 5, Fig. 1), which follows the trend observed in viscosity measurements (Table 4). A feature of the molecular weight distributions is the decrease in polydispersities ($\bar{P}_w/\bar{P}_n$) as the molecular weight decreases.

For the autohydrolysed-extracted pulps P1–P5 from *E. regnans*, there is a decrease in molecular weight and polydispersities as the autohydrolysis time increases (Table 5, Fig. 2). The samples P1 and P2 which had been autohydrolysed for 5 min at 200°C had higher viscosities and $\bar{P}_w$ values than the commercial sample Viscokraft, but had lower $\bar{P}_n$ and polydispersity values. This is also reflected in the low α-cellulose values found for autohydrolysed–exploded–extracted pulps (Table 1) compared to the high value measured for Viscokraft (95·4%). Thus the samples P1 and P2 do not have the molecular weight characteristics of the commercial cellulose, in spite of having slightly higher viscosities. The pulps P3–P5 autohydrolysed for longer periods had lower molecular weights than the Viscokraft sample.

Table 4. Characteristics of commercial celluloses

	Cuene viscosity (mPa s)	α-Cellulose	Pentosan (%)
Acetakraft	11·2	97·8	1·3
Viscokraft	4·52	95·4	1·9
Avicel	2·10		1·9

Table 5. Molecular weight data on cellulose tricarbanilates

Cellulose	$\bar{P}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$
Acetakraft	2 110	362	5·8
Viscokraft	1 010	267	3·8
Avicel	241	75	3·2
E. regnans[a]			
P1	1 100	184	6·0
P2	1 290	170	7·6
P3	769	132	5·8
P4	485	108	4·5
P5	515	111	4·6

[a] Chlorite-delignified autohydrolysed-extracted pulps.

CONCLUSIONS

Explosive release of *E. regnans* woodchips autohydrolysed at 200°C from the Siropulper pilot plant gave pulp with similar yield and chemical composition to that of a non-exploded sample.

Sodium hydroxide solution was the most effective medium of those tested for extraction of lignin from the *E. regnans* autohydrolysed pulps, and extraction at 100°C with 0·33 M NaOH gave pulps with Kappa numbers 35–45. The efficacy of extraction at 20°C decreased in the order 0·125 M NaOH > 50% aqu. NH_3 > 0·2% $Ca(OH)_2$. For organic solvents, the efficacy of extraction at 60°C was in the order 70% aqu. ethanol > acetone > ethanol.

E. regnans cellulose samples prepared from wood which had been autohydrolysed for 5 min at 200°C had higher viscosities than a commercial viscose-grade cellulose. However, the former samples had higher polydispersities and lower α-cellulose values.

Conventional prehydrolysis-alkali pulping of the *E. regnans* sample gave pulps with properties of an acetylation-grade cellulose.

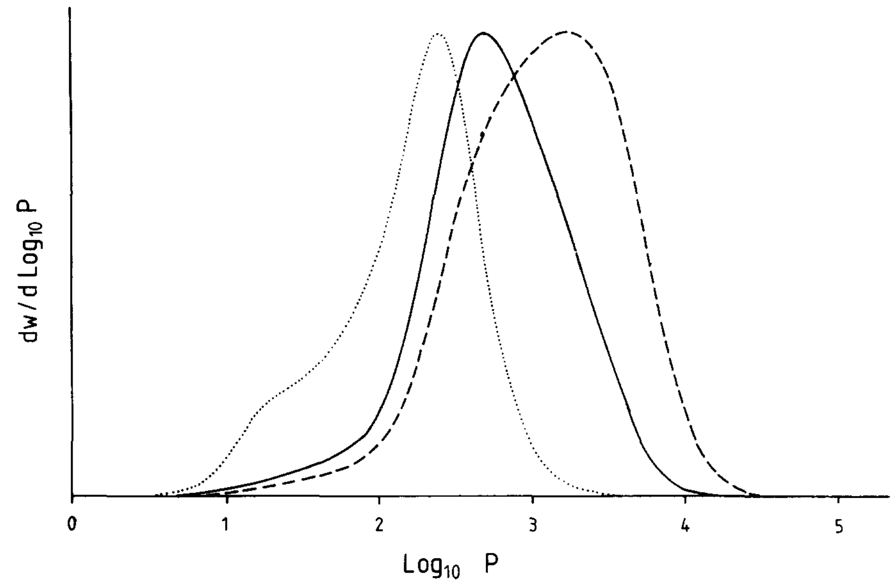

Fig. 1. Differential mass distributions by HPSEC of tricarbanilates derived from commercial cellulose samples: - - -, Acetakraft; ——, Viscokraft; ·······, Avicel PH-101.

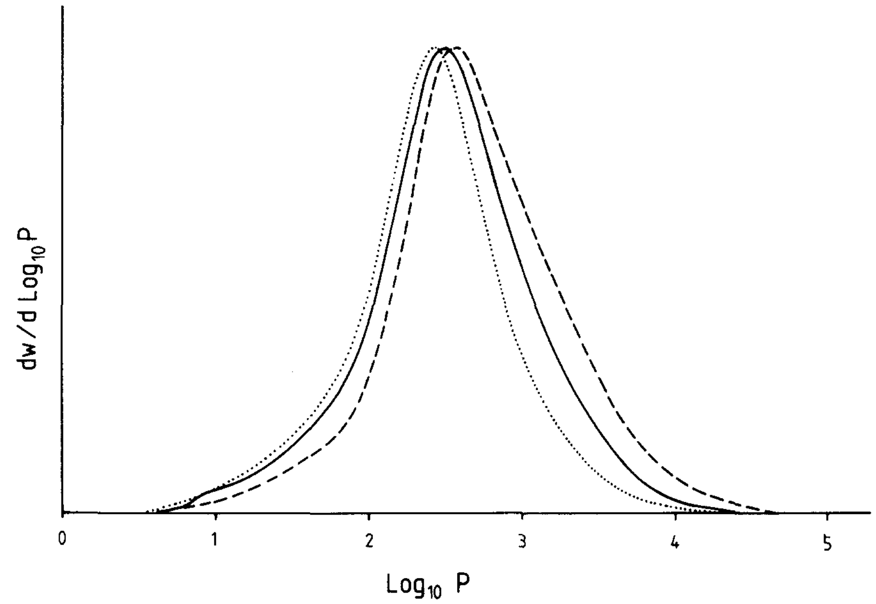

Fig. 2. Differential mass distributions by HPSEC of tricarbanilates derived from *E. regnans* cellulose by autohydrolysis-explosion-extraction. Autohydrolysis time: - - -, 5 min (P2); ——, 10 min (P3); ·······, 20 min (P5).

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