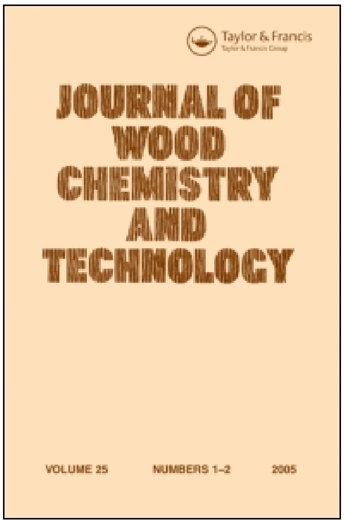

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CHARACTERIZATION OF THE SOLID RESIDUES OF THE SUPERCRITICAL EXTRACTION OF POPULUS TREMULOIDES IN METHANOL

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ABSTRACT

Data are reported for the chemical analysis of the solid residues of supercritical extraction of Populus tremuloïdes in methanol. The lignin content is determined by the thioglycolic acid test as the Klason test is shown to yield an estimation of recondensed material in addition to lignin. The TFA acid hydrolyzates of SCE solid residues were analysed for simple sugars by HPLC. The results indicate that hydrolyzable material contains products of thermal degradation of polysaccharides.

INTRODUCTION

In the recent studies of thermal and thermochemical processes of wood liquefaction, considerable progress has been reported in the analysis of gaseous and liquid products (1-5). Less attention has been given to the composition of the solid products, apart from their elemental analysis (6). These solids have been analyzed by techniques derived for the characterization of lignin, cellulose and hemicellulose in wood (7-8a). A rapid thermal analysis technique for the determination of residual lignin and holocellulose has

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also been proposed (9) and demonstrated for solids thermally degraded at temperatures not exceeding 240°C.

In this paper we report our efforts to characterize the solid residues produced in a series of experiments for the semicontinuous extraction of Populus tremuloïdes in supercritical methanol (10), at temperatures ranging from 250 to 350°C (Supercritical Extraction residues or SCE residues).

The methods selected for lignin determination in this study were the Klason lignin test and the thioglycolic acid lignin test, both techniques being completed by extensive IR and elemental analyses. The lignin in SCE residues was further characterized by the production of aldehydes as determined by the nitrobenzene oxidation technique. Residual carbohydrates were analyzed using a HPLC determination of the sugars produced by hydrolysis of the SCE residues with trifluoroacetic acid.

It is hoped that a critical comparison of the results of these various analytical techniques, most of which have been derived for wood characterization, would allow conclusions to be drawn concerning their applicability to solids derived from wood by thermal degradation.

EXPERIMENTAL PROCEDURE

1. Supercritical Extraction Procedure: About 30 g of wood from the stem of a 20 year Populus tremuloïdes was cut as regular parallelepipeds (5x5x2 mm^3) and introduced in a 150 ml tubular reactor with 100 ml of cold methanol (10). The closed reactor is first heated to 100°C in about half an hour before hot flowing methanol

(temperatures 250-350°C) is admitted in the system. The pyrolytic oils so produced are thus quickly withdrawn and thus not allowed to recondense on the solid material. This extraction is completed in less than three hours. At that time, the reactor is evacuated while the reactor is maintained at the temperature of the experiment.

2. Klason Lignin Test: The tests for wood and solid residues were performed according to TAPPI Standard T13 method. The residue, obtained by this procedure and designated hereafter as the Klason residue, was dried at 105°C for 2 hours. The Klason residue was then expressed in wt% based on initial weight of the dry wood sample.

3. Thioglycolic Acid Lignin Test: The test was performed following the procedure of Holmberg (11a). One gram of sample was pre-extracted and put in a solution of 1 g thioglycolic acid (supplied by Aldrich Chemical Co.) in 10 ml 2N HCl, and heated on a water bath with occasional shaking for about 4 hours. After cooling the solution was filtered and the residue was washed with distilled water. The air-dried residue was then treated with 50 ml of 95% ethanol at room temperature for 48 hours, then filtered and dried in air. The filtrate was evaporated completely leaving behind a residue designated hereafter as the thiolignin-1 (TL-1). The solid residue of filtration, after alcohol extraction, was stirred for 24 hours at room temperature with 50 ml of 0.5N NaOH and the mixture was filtered and washed with 50 ml of distilled water. The filtrate was acidified with 5N HCl and an additional amount, designated as the thiolignin-2 (TL-2), was separated as a

precipitate after standing overnight. Total thiolignin (TL) was the summation of TL-1 and TL-2. Both thiolignins were dried at 25-30°C under a constant nitrogen flow, then weighed and expressed in wt% based on initial dry wood.

4. IR Spectroscopy: The infrared spectra of Klason residues, TL-1 and TL-2 were recorded with an IR spectrophotometer Beckman IR 425. KBr disks (1 mg sample in 350 mg KBr) were prepared for the solid Klason residues and TL-2, whereas KBr windows were used for the viscous TL-1.

5. Elemental Analysis: Carbon, hydrogen and nitrogen content of wood, SCE residues, Klason residues, TL-1 and TL-2 were determined with an F & M Scientific 185 C,H,N Analyzer from Hewlett-Packard. The elemental analyses for oxygen in TL-1 and TL-2 were carried out on a Perkin-Elmer 240B Elemental Analyzer.

6. Carbohydrates Analysis: Carbohydrates from wood and SCE residues were hydrolyzed with trifluoroacetic acid (TFA acid, supplied by Aldrich Chemical Co.) following the method described by Fengel and Wegner (12). A dry pre-extracted sample (100 mg) was put in 10 g of TFA and the mixture was kept overnight at ambient temperature for swelling. The mixture was heated in an oil bath under reflux for 1 hr before diluting to 80% w/w TFA and refluxed again for 15 min. The solution was then diluted to 30% w/w TFA acid and refluxed for 2 hours. The solution was filtered and the residue was washed with about 100 ml of water. The filtrate was then evaporated in a rotatory vacuum evaporator at 50°C; about 30 ml of water was added to the dry material and the solution was again

evaporated as before. This procedure was repeated 5 times to remove all TFA acid in the final hydrolyzed material. Then this product was dissolved in water to perform the characterization by HPLC. The solid residue obtained in this hydrolysis process was dried and weighed.

The HPLC analysis was made with a Perkin-Elmer 3B chromatograph, using a HC-40 cation exchange resin, Ca^{++} form, column from Hamilton and a Refractive Index LC-25 from Perkin-Elmer as detector. The operating conditions were a column temperature of 80°C, HPLC grade water as the mobile phase delivered with a flow rate of 0.6 ml/min and an injection volume of 5µl. The HPLC column was calibrated with D-cellobiose, D-(+)-glucose, D-(+)-xylose, D-(+)-galactose and D-(-)-arabinose (all from Aldrich Chemical Co.).

7. Nitrobenzene Oxidation: The nitrobenzene oxidation was performed according to Hardell et al. (13). The wood residue (20 mg) in 2 ml 2N NaOH was heated at 180°C for 2 hours with 200 µl nitrobenzene. The oxidation products were isolated by extraction with methylene chloride and ethyl ether (14). The amounts of vanillin and syringaldehyde were determined by GLC using methyl vanillate as an internal standard; the column was 5% OV-1 on Gas Chrom Q 100/120 at a temperature of 150°C using He as carrier gas (Reagent and standards from Aldrich Chemical Co.).

RESULTS

TABLE 1 presents the SCE conditions, yields of oil and solid residue in addition to the analytical results such as quantity of

TABLE 1

Percentages of Oil Yield and Solid Residue in Supercritical Extraction. Percentages of Klason Residue, Thioglycolic acid lignin and Recondensed Material in SCE Solid Residues.

Sample	Supercritical extraction conditions			SCE Solid Residue(wt%)	Oil yield wt%	Pre-extractive wt%	Klason residue (wt%)	TFA solid residue (wt%)	TGAL wt%	% conversion of lignin	Recondensed material wt%
	Temperature °C	Pressure Psi	Flow rate L/h.								
P.tremuloides						4.43	17.60	17.05	15.61		
MP-22	250	500	1.5	74.8	11.7	1.42	19.54	20.41	10.72	31.33	8.82 ± 1.48
MP-17	250	1500	2.5	69.7	28.0	1.63	7.37	5.37	4.51	70.47	2.86 ± 1.38
MP-6	250	1500	0.5	55.4	21.4	3.48	16.85	16.35	12.30	21.20	4.55 ± 1.10
MP-15	250	2500	1.5	68.4	25.8	2.22	5.16	4.12	3.70	76.30	1.42 ± 1.36
MP-16	300	500	0.5	40.5	19.5	4.15	17.12	17.54	4.89	68.99	12.23 ± .81
MP-20	300	500	2.5	31.0	18.0	2.55	24.18	22.89	3.79	75.72	20.39 ± 0.62
MP-9	300	1500	1.5	16.4	42.1	1.07	15.09	14.51	0.73	94.94	14.39 ± .33
MP-21	300	1500	1.5	15.7	39.9	1.29	13.97	14.03	0.66	95.77	13.31 ± .31
MP-12	300	1500	1.5	15.9	42.0	0.96	14.68	14.68	0.57	96.35	14.11 ± .32
MP-13	300	2500	0.5	18.4	44.0	1.89	12.05	12.00	1.10	92.95	10.95 ± .37
MP-18	300	2500	2.5	15.0	49.8	1.41	13.02	13.02	0.84	94.62	12.18 ± 0.30
MP-27	330	2500	1.2	8.4	-	0.67	5.95	6.12	0.40	97.44	5.57 ± .16
MP-14	350	500	1.5	26.9	30.2	1.21	24.23	22.71	1.41	90.97	22.82 ± 0.54
MP-11	350	1500	0.5	18.2	46.0	0.70	16.77	17.35	0.70	95.52	16.07 ± .36
MP-8	350	1500	2.5	10.2	57.5	0.00	9.69	10.08	0.59	96.22	9.10 ± 0.20
MP-24	350	2500	1.5	6.1	54.5	1.01	4.85	4.9	0.19	98.78	4.66 ± .12

wt% based on initial dry wood

pre-extractive, Klason residue, TFA residue, thioglycolic acid lignin and recondensed material. After each SCE experiment, the solid residue was dried in oven at 105°C and oil was separated from the solvent and water using a rotatory vacuum evaporator at 60°C (10). Both solid residue and oil yields are expressed in weight percent (wt%) on the basis of initial dry wood. The mass of extractives in wood and solid residues, separated following the procedure described in the experimental section dealing with the Klason test, were determined by evaporating the extraction solvent at 25-30°C under a constant nitrogen flow. They are also expressed in wt% on the basis of initial dry wood. The lignin content of P. tremuloïdes determined by the Klason method was found to be of 17.6 wt%, which is good agreement with the values reported by Wayman et al. (8b) and Roy et al (15), 17.6 and 18.0 wt% respectively. Similarly, the mass of the Klason residue separated from SCE solid residue was determined and expressed in TABLE 1 as wt% of initial dry wood.

TABLE 1 gives also the wt% of TFA acid solid residues from wood and SCE residues. These were determined by difference between the mass of pre-extracted material and the mass of dried hydrolyzed TFA acid carbohydrates.

Thiolignins obtained from wood and SCE residues by the thioglycolic acid lignin method are derivatives of lignins and thioglycolic acid. The elemental analysis of TL-1 and TL-2 and their masses expressed in wt% of dry wood are shown in TABLE 2. The values of %C, %H, %O and %S are close to the corresponding values

TABLE 2

Elemental Analysis of Thiolignin -1 and -2.

SAMPLE	Thiolignin -1					Thiolignin -2				
	mass wt%	%C	%H	%O	%S	mass wt%	%C	%H	%O	%S
wood	3.85	58.09	8.30	24.79	8.82	16.50	56.46	6.09	28.99	8.46
MP-22	4.16	64.78	8.40	19.22	7.6	9.10	63.26	4.90	23.55	8.29
MP-17	2.57	69.10	10.78	18.37	1.75	2.88	60.30	5.50	26.29	7.91
MP-6	3.27	68.42	8.77	20.29	2.52	12.27	61.94	5.37	26.05	6.64
MP-15	2.35	70.88	10.29	17.27	1.56	1.96	59.66	5.71	26.47	8.16
MP-16	2.54	65.34	9.21	21.27	4.18	5.18	57.21	4.75	19.96	18.08
MP-20	1.99	60.88	9.35	22.41	7.36	4.44	56.00	4.57	20.63	18.80
MP-9	1.08	55.06	8.30	22.64	14.00	0.07	-	-	-	-
MP-21	1.07	54.78	8.82	21.91	14.49	0.02	-	-	-	-
MP-12	1.05	57.19	8.78	17.29	16.74	0.003	-	-	-	-
MP-13	0.58	-	-	-		1.09	57.54	5.51	27.65	9.3
MP-18	0.63	-	-	-		0.35	-	-	-	-
MP-27	0.59	65.23	9.19	19.22	6.36	0.28	63.40	5.23	18.65	12.72
MP-14	1.23	53.57	7.93	23.50	15.00	0.91	59.60	5.92	25.26	9.20
MP-11	1.01	56.39	7.82	24.41	11.38	0.00	-	-	-	-
MP-8	0.60	-	-	-		0.00	-	-	-	-
MP-14	0.22	58.97	8.97	19.86	12.20	0.004	-	-	-	-

*wt% based on initial dry wood.

obtained by Holmberg (11b) for Populus tremuloïdes. In several experiments with SCE residues the amount of thiolignin was too small for an elemental analysis to be performed, especially when as for experiments MP-13, 18 and 8, KBr pellets for IR spectroscopy had also to be prepared.

According to Freudenberg (16), about two-thirds of the thioglycolic acid units attach to the lignin by cleavage of ether bonds, while the other one-third substitutes hydroxyls in the lignin as $C_2H_3O_2S$ groups. Thus the masses of carbon, hydrogen and oxygen in thioglycolic acid lignin in X grams of thiolignin are given by:

$$\text{Carbon (g)} = X\ \text{(g)}\ (\%C - (0.749\ \%S))\ /\ 100,$$

$$\text{Hydrogen (g)} = X\ \text{(g)}\ (\%H - (0.105 \times \%S))\ /\ 100,$$

$$\text{Oxygen (g)} = X\ \text{(g)}\ (\%O - (0.831\ \%S))\ /\ 100,$$

where %C, %H, %O and %S are determined by elemental analysis of thiolignins and reported in TABLE 2.

The thioglycolic acid lignin (TGAL) contents of SCE residues expressed in wt% on the basis of initial dry wood are reported in TABLE 1. The TGAL content in P. tremuloïdes wood was determined as 15.6 wt% (thiolignin content was 20.35% which is close the value of 22.0% found by Holmberg (11)).

The values reported in TABLE 1 for the conversion of lignin were calculated with respect to the TGAL content:

$$\%\text{conversion} = 100\ (\text{TGAL in wood} - \text{TGAL in SCE residue})\ /\ \text{TGAL in wood}.$$

The difference between the mass of Klason residue and that of TGAL in the same SCE residue represents the mass of a material which is not hydrolyzed in 72% H_2SO_4 and which is not lignin. We designated this as the recondensed material. The wt% of this recondensed material, expressed on dry wood basis, is also reported in TABLE 1 along with an estimation of percent error. This error is mainly due to the difference in the estimations of lignin content in wood using the Klason test and the thiolignin procedure.

The elemental analysis of SCE residues and Klason residues were also performed and the values of H/C and O/C ratios are shown in TABLE 3. The values of H/C and O/C atomic ratios for TGAL-1 and TGAL-2 are also shown in the same table. The elemental analyses of recondensed material were derived by difference from the elemental analyses of Klason residue and TGAL by making separate material balances for carbon, hydrogen and oxygen. The ratios of H/C and O/C for recondensed material are given in TABLE 3. The values of H/C and O/C ratios of recondensed material for experiments MP-17, 6 and 15 are not reported in TABLE 3, as for these three experiments the calculated masses of H, C and O were within experimental errors.

The masses of carbohydrates separated from wood and SCE residues by hydrolysis both with TFA and sulfuric acids are presented in TABLE 4. Both methods give results in close agreement. The TFA acid hydrolyzed products were separated by HPLC. By injecting the mixture of standard sugars, it was observed that the column HC-40 cannot separate xylose, galactose and arabinose which give a single peak. In the experimental results, this single peak was considered as due to xylose, since in wood samples the quantity of galactose and arabinose is very small compared to xylose (17). The

TABLE 3

H/C and O/C Ratios of SCE Residues, Klason Residues, Thioglycolic Acid Lignins -1 and -2 and Recondensed Material.

Sample	Solid residue and wood		Klason residue		TGAL-1		TGAL-2		Recondensed Material	
	H/C	O/C	H/C	O/C	H/C	O/C	H/C	O/C	H/C	O/C
wood	1.69	0.77	1.02	0.37	1.72	0.25	1.24	0.33		
MP-22	1.40	0.66	0.95	0.31	1.54	0.16	0.85	0.22	0.81	0.48
MP-17	1.73	0.81	0.93	0.40	1.87	0.19	1.03	0.27	-	-
MP-6	1.18	0.57	0.77	0.42	1.53	0.21	0.98	0.27	-	-
MP-15	1.89	0.83	1.04	0.33	1.74	0.17	1.09	0.28	-	-
MP-16	1.08	0.33	0.81	0.21	1.69	0.21	0.63	0.08	0.70	0.24
MP-20	0.81	0.18	0.45	0.17	1.85	0.22	0.74	0.09	0.32	0.18
MP-9	0.76	0.16	0.64	0.18	1.84	0.15	-	-	0.58	0.19
MP-21	0.80	0.14	0.71	0.15	1.99	0.13	-	-	0.65	0.15
MP-12	0.70	0.14	0.56	0.20	1.89	0.04	-	-	0.50	0.20
MP-13	1.01	0.34	0.76	0.27	-	-	1.15	0.36	-	-
MP-18	0.85	0.22	0.67	0.30	-	-	-	-	-	-
MP-27	0.98	0.19	0.78	0.19	1.69	0.14	0.87	0.09	0.69	0.19
MP-14	0.70	0.20	0.59	0.13	1.80	0.20	1.13	0.25	0.54	0.12
MP-11	0.70	0.10	0.68	0.14	1.66	0.23	-	-	0.64	0.14
MP-8	0.50	0.02	0.41	0.06	-	-	-	-	-	-
MP-24	0.78	0.18	0.73	0.13	1.85	0.15	-	-	0.70	0.13

TABLE 4

Analysis of hydrolyzates.

Sample	SCE Solid Residue wt%	Hydrolyzate (TFA method) wt%	Hydrolyzate (H_2SO_4 method) wt%	Glucose wt%	Xylose wt%	Hydrolyzate - (Glucose + xylose) wt%
wood	100	78.52	77.97	47.60	27.16	3.76
MP-22	74.8	52.97	53.84	34.22	13.45	5.30
MP-17	69.7	62.70	60.70	26.46	13.42	22.82
MP-6	55.4	35.57	35.34	21.13	7.11	7.33
MP-15	68.4	62.06	61.02	18.43	8.44	35.19
MP-16	40.5	18.81	19.23	10.48	3.24	5.09
MP-20	31.0	5.56	4.27	-	-	
MP-9	16.4	0.82	0.24	0.00	0.00	0.82
MP-21	15.7	0.38	0.44	0.00	0.00	0.38
MP-12	15.9	0.26	0.26	0.10	0.00	0.16
MP-13	18.4	4.51	4.46	1.90	0.60	2.51
MP-18	15.0	0.57	0.57	0.07	0.00	0.50
MP-27	8.4	1.62	1.78	0.55	0.00	1.07
MP-14	26.9	2.98	1.46	1.33	0.35	1.30
MP-11	18.2	0.15	0.73	0.00	0.00	0.15
MP-8	10.2	0.12	0.51	0.00	0.00	0.12
MP-24	6.1	0.19	0.24	0.00	0.00	0.19

*wt% based on initial weight of dry wood.

results for the masses of hydrolyzed glucose and xylose expressed as wt% of dry initial wood are shown in TABLE 4.

The infrared spectra of Klason residues obtained from wood and those obtained from the SCE residues MP-22, 16, 18 and 14 are shown in FIGURE 1. The infrared spectra of the Klason residue from wood shows all of the lignin characteristic bands (18) such as bands at 1600, 1490-1510 and 1415 cm^{-1} due to aromatic skeletal vibrations, 1450 cm^{-1} due to asymmetric C-H deformation in methyl and methylene groups, 1310 cm^{-1} due to C-O stretching in condensed guaiacyl unit, 1210 cm^{-1} due to C-O stretching in syringyl and guaiacyl units, 1110 cm^{-1} due to aromatic C-H in plane deformation contributed from both syringyl and guaiacyl units, 1015 cm^{-1} due to aromatic C-H in plane deformation, assigned as characteristic of uncondensed guaiacyl units and 905 cm^{-1} due to aromatic C-H out of plane deformation of syringyl unit. The infrared spectrum of the Klason residue obtained from MP-22 also shows all the lignin characteristic bands. But with the increase of SCE temperature, the Klason residue shows from fewer to no lignin characteristic bands. The infrared spectra of TL-1 obtained from wood and SCE residues MP-22, 16 and 14 are shown in FIGURE 2. From this figure it is observed that all the thiolignins from SCE residues show the same characteristic bands of lignin as those displayed by the spectrum of TL-1 obtained from wood. This was also observed for TL-2.

The most important difference between these thiolignin spectra and the spectrum of Klason residue from wood is the presence of an intense band at 1720 cm^{-1} ascribed to the carboxyl stretching from

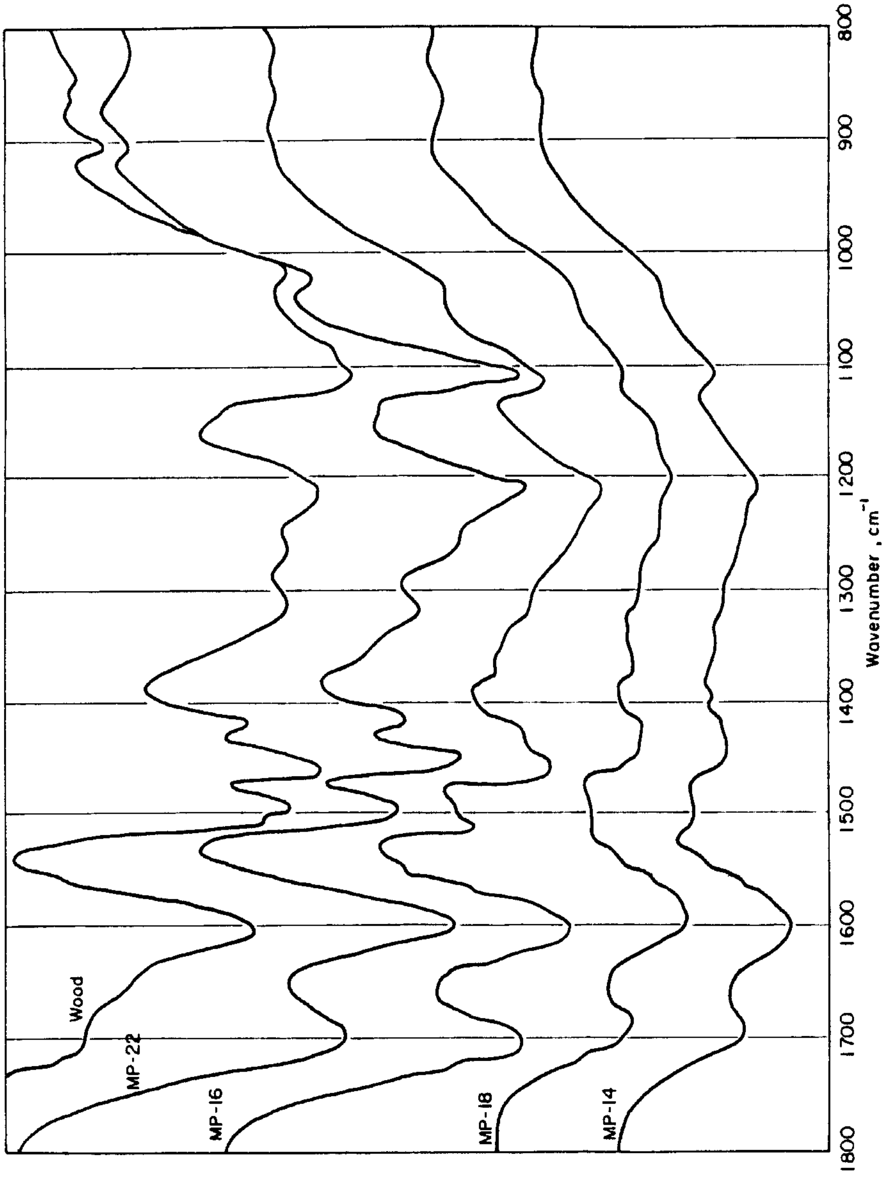


FIGURE 1. Infrared spectra of Klason residues.

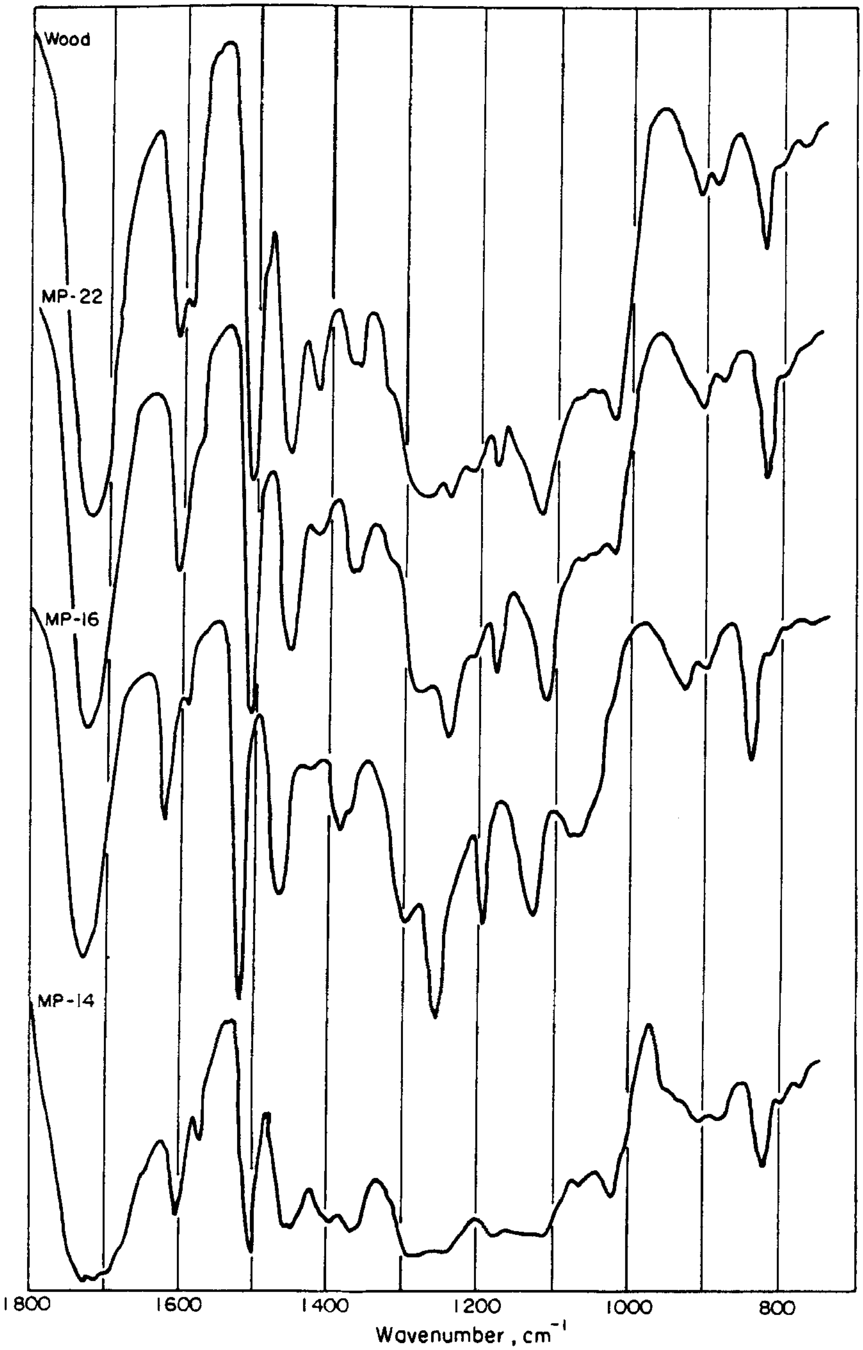


FIGURE 2. Infrared spectra of Thiolignins-1.

thioglycolic acid. A series of bands at 825-930 cm^{-1} are also observed in the spectra of TL-1 (FIGURE 2) and not in the spectrum of Klason residue (FIGURE 1). Weak bands at 825, 890 and 925 cm^{-1} are detected in the IR spectra of thioglycolic acid. In the region 1100-1400 cm^{-1} bands from thioglycolic acid are also overlaping with the lignin bands.

Some of the lignin containing SCE residues have been submitted to the nitrobenzene oxidation test with special interest being focused on the determination of vanillin and syringaldehyde (MP 17, 6, 15, 16 and 20). The total amount of these two aldehydes was much lower than the 15% value expected on the basis of the total lignin content (8a). The S/V molar ratio was found to be in the range 1.7 to 2.6 which is higher than the 1.32 value usually encountered in recondensed lignin.

DISCUSSION

The Klason residue data presented in TABLE 1 show that at the three temperatures investigated, conditions can be found where the Klason residue from SCE solids is higher than the lignin initially present in the wood. This result is a definite proof of the inadequacy of the Klason test to determine the amount of unconverted lignin in thermally degraded wood samples. Obviously the Klason residue as well as the residue from TFA acid hydrolysis, contains some solid products of thermal degradation which cannot be hydrolyzed.

In the thioglycolic acid lignin test, lignin is dissolved in the thioglycolic acid solution, a process which is not liable to happen with recondensed products. Therefore one would expect the thioglycolic acid test to be more appropriate for the determination of lignin in SCE residues. Indeed the data for TGAL in TABLE 2 do not present the same peculiarities as the Klason data. This is confirmed by the lignin conversion curves calculated from these TGAL and shown in FIGURE 3. These curves show regular increases in lignin conversion with temperature at 500 and 2500 psi. From the TGAL data in TABLE 1, it is also apparent that solvent flow rate during the extraction has a large effect only at 250°C.

The difference in nature between the Klason residue and the material extracted in the thioglycolic acid test is further demonstrated by a comparison between the IR spectra of Klason residues (FIGURE 1) and those of thiolignin 1 (FIGURE 2) for the same SCE solids.

It is known that during isolation of Klason lignin in wood, some condensation occurs and therefore that this lignin should be considered as a condensed lignin (18,19). However the IR spectra of the Klason lignin isolated from Populus tremuloïdes (FIGURE 1) shows clearly its lignin-like nature in spite of some condensation (bands at 1595, 1505, 1325, 1275, 1235, 1130, 1030, 915 and 835 cm^{-1}). From the IR spectra for the Klason residues of SCE solids (FIGURE 1) it is apparent that the Klason residues lose their lignin-like nature as the temperature of extraction increases. As observed by Wayman for residual autohydrolysis lignin obtained from aspen wood at 195°C (8a), a $C = O$ group (band at 1700 cm^{-1}) due to an unconjugated open chain ketone group or an aryl/α, β unsaturated

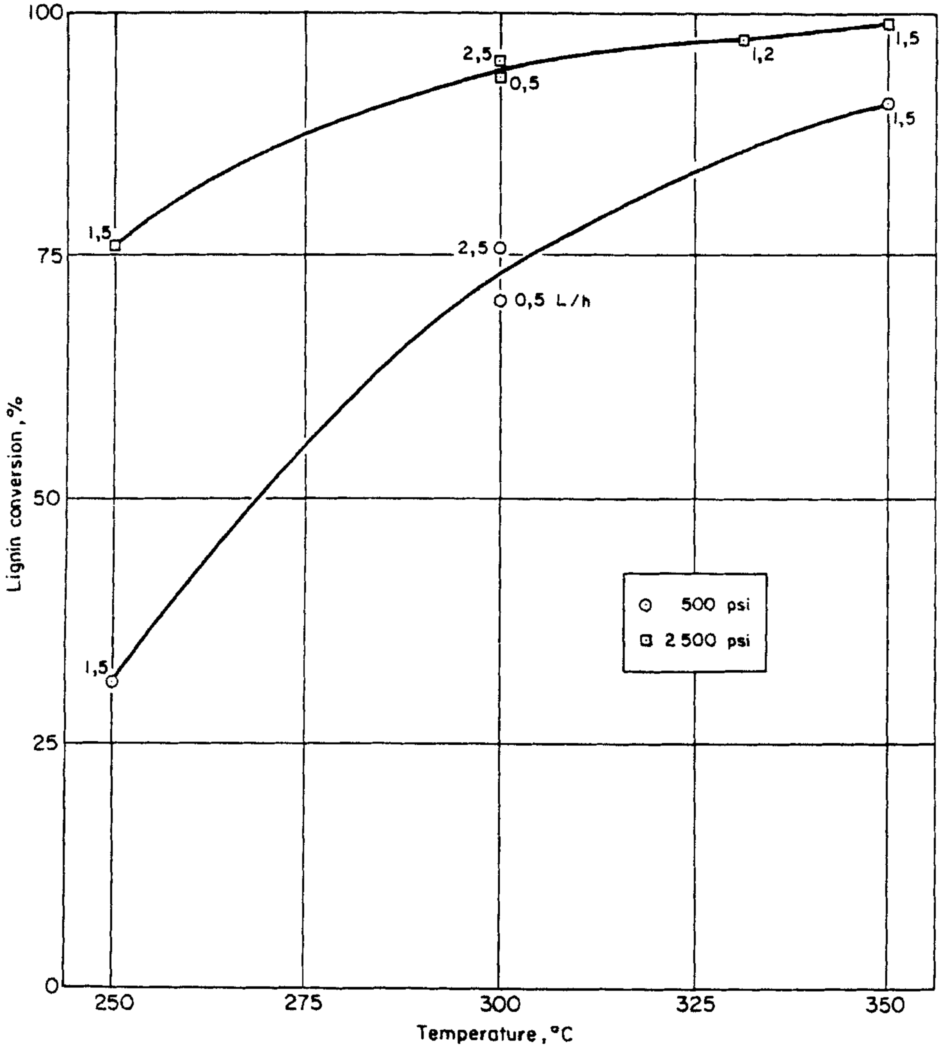


FIGURE 3. Lignin conversion as a function of the temperature of extraction.

ester/acid, appears in the spectra of the Klason residues as the temperature of extraction increases.

By contrast, FIGURE 2 shows that thiolignins extracted from SCE residues keep the characteristic features of lignin in their IR spectra. This is specially true for the bands close to 1600 and 1500 cm^{-1} while all other lignin bands are discernible in spite of some overlap with features of the thioglycolic acid spectrum.

This confirms our belief that the thioglycolic acid test is a suitable method for the determination of uncondensed lignin in SCE residues. In spite of the fact that

1) the Klason test induces some condensation reactions,

2) the thioglycolic acid test may only extract those lignin fragments containing benzyl alcohol groups or aryl ether groups (18),

we would like to suggest

1) that the thioglycolic acid lignin represents a good estimate of unconverted lignin,

2) the Klason residue represents the summation of unconverted lignin and of condensation products formed by pyrolysis reactions during the SCE process.

As a consequence we suggest that the difference between the Klason residue and the thioglycolic acid lignin is representative of recondensed material in SCE residues.

FIGURE 4 shows the variations of the mass of recondensed material in SCE residues with the conditions of supercritical extraction. These curves suggest that at least two phenomena are governing the amount of recondensed material. The first one is the only one to be operative between 250 and 300°C. It is a production of recondensed material, the rate of which increases with temperature and decreases with the pressure of the solvent. This last effect suggests a competition between the condensation reaction and extraction of the reactants. At temperatures higher than 300°C a secondary reaction seems to consume the condensed material at a rate which depends very much on the pressure of the solvent and its flow rate.

FIGURE 5 shows the percentage of condensed material plotted as a function of lignin conversion. This graph suggests different condensation reactions at 250°C and at 300-350°C. At 250°C in particular, the condensation seems to be a secondary reaction of lignin conversion. As also shown on the figure, for several experiments the percents of condensed material are higher than the value which would be calculated assuming that all converted lignin is transformed to condensed material (line A). We believe that this indicates that the condensation reaction involves not only the products of degradation of lignin but also those of carbohydrates.

FIGURE 6 shows a comparison of the elemental analysis results for SCE residues, thioglycolic acid lignins in thiolignins 1 and 2 and recondensed material. The rather narrow ranges found for H/C and O/C in both TGAL are indicative of the unchanged nature of the lignin extracted in the thioglycolic acid test. The observed values are in agreement with the literature (11b). For the condensed material at 300 and 350°C narrow ranges are also found for H/C and O/C averaging at 0.55 for H/C and 0.15 for O/C. These low values

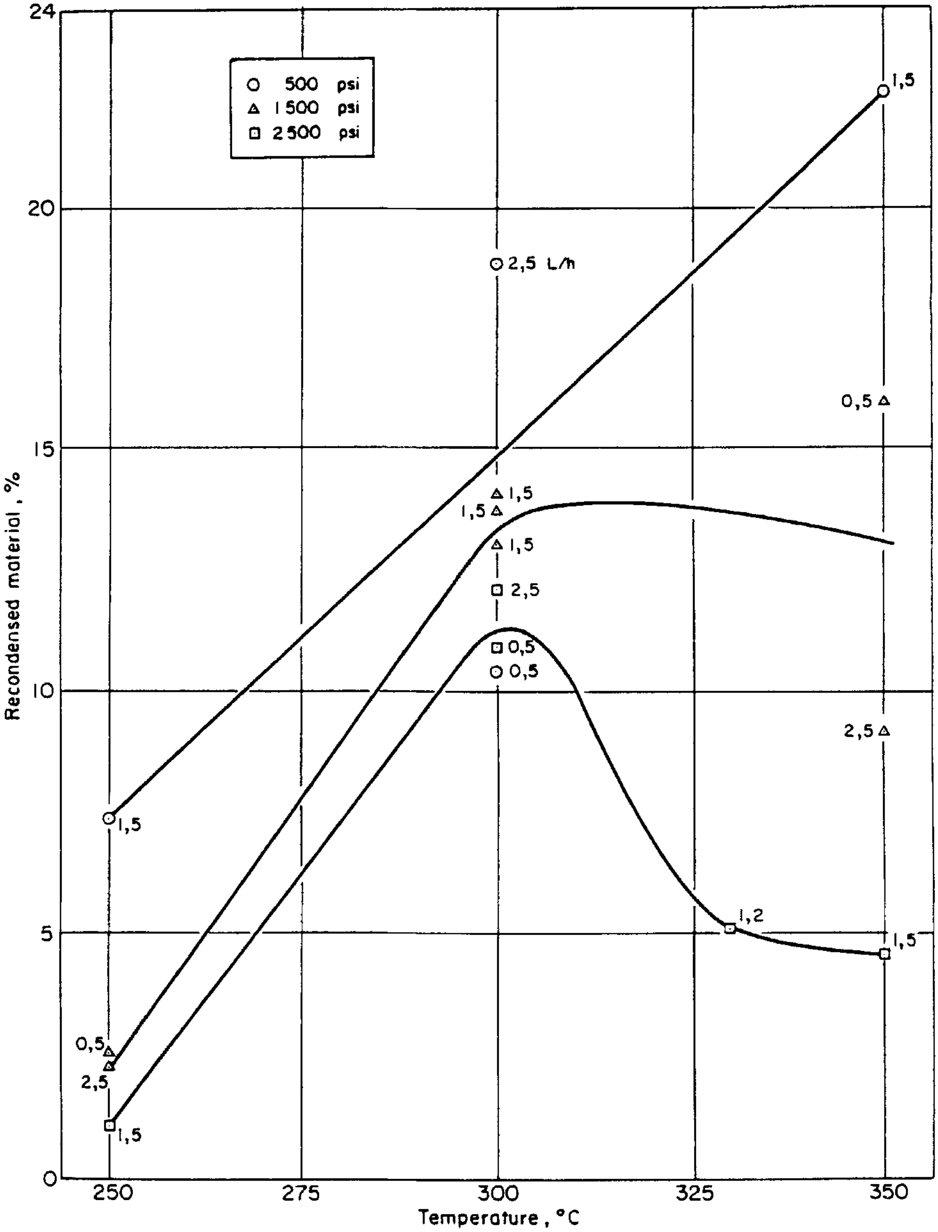


FIGURE 4. Effect of SCE conditions on recondensed material.

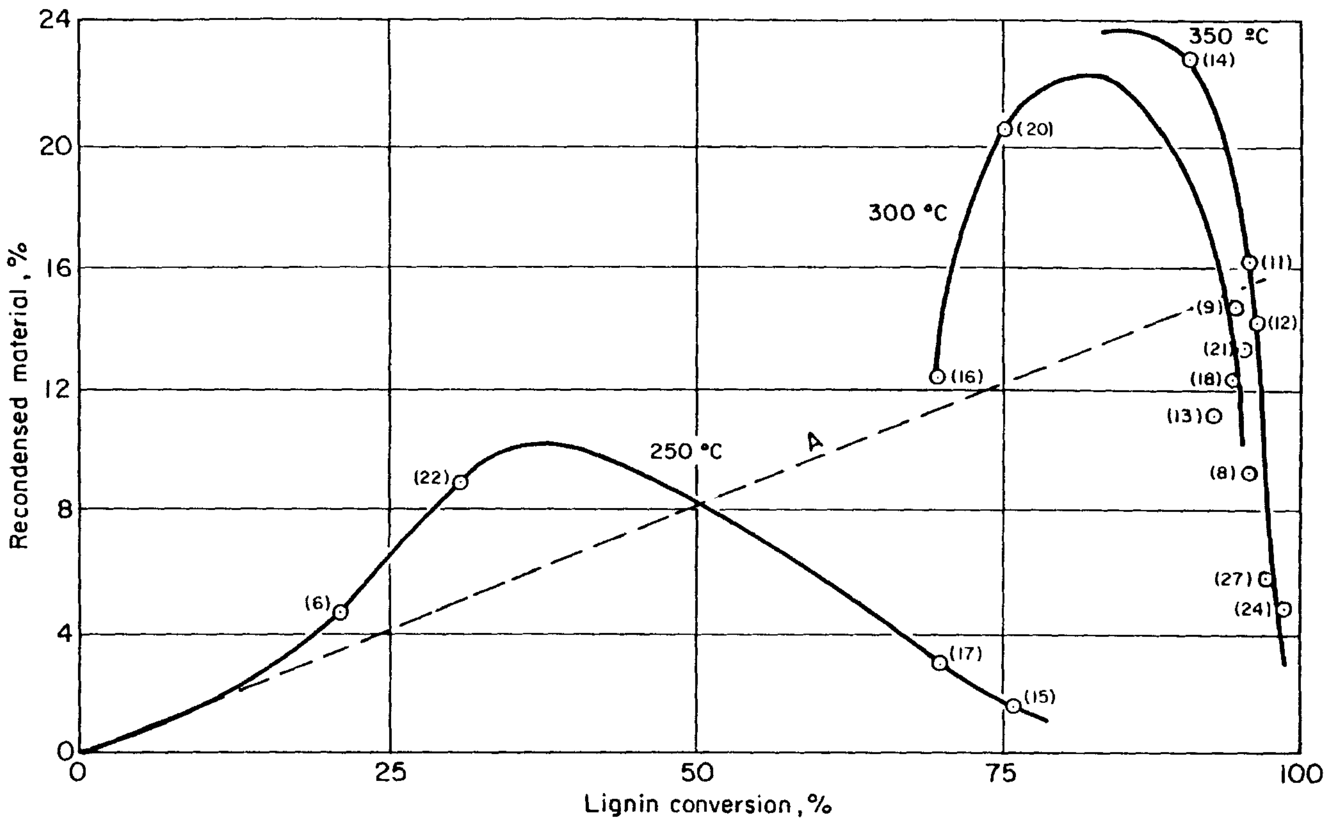
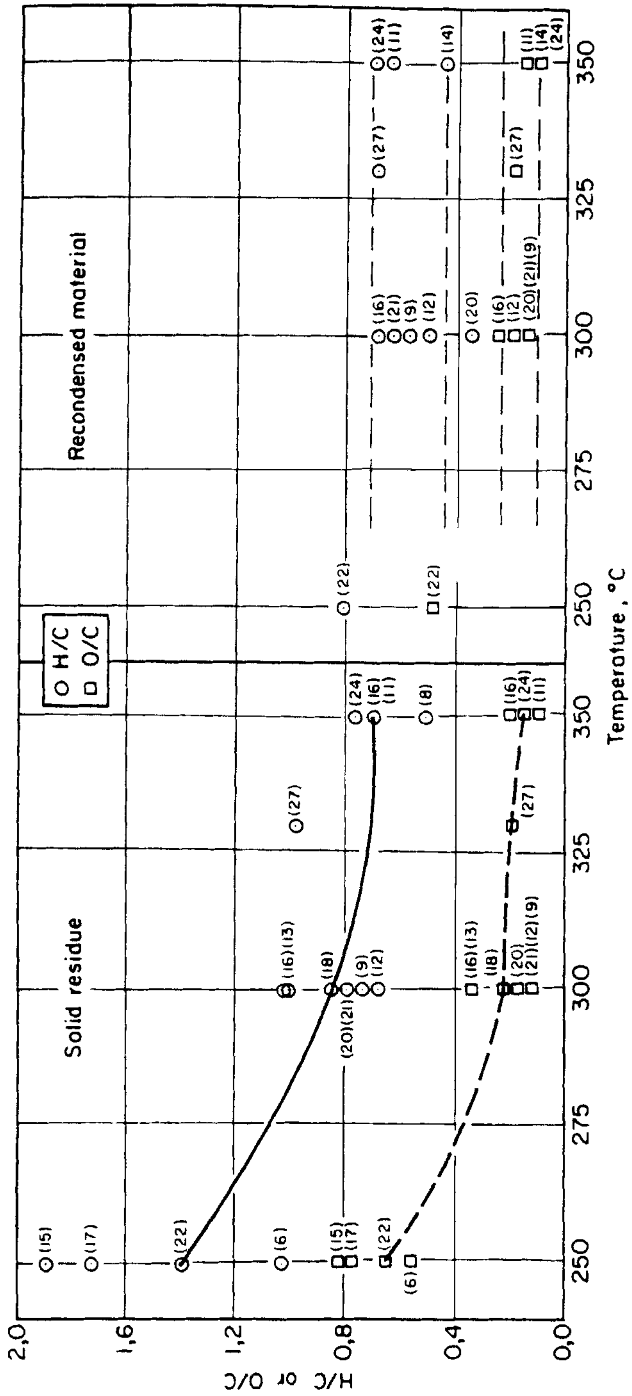


FIGURE 5. Recondensed material as a function of lignin conversion.

suggest a highly recondensed material probably containing polyaromatics. Only one significant point could be obtained at 250°C showing higher values for H/C (0.8) and O/C (0.48). This is an indication of the difference in chemical nature of the condensed material obtained at 250°C compared to the one formed at 300-350°C.

TABLE 4 reports data on TFA acid hydrolysis of wood and SCE residues and on the chromatographic analysis of the hydrolyzates. The percent of hydrolyzed material in the Klason test are also reported, showing a good agreement between the two methods. FIGURE 7 gives some typical chromatograms of hydrolyzates which show that in addition to glucose and xylose at least two other major products can be present in the TFA acid hydrolyzed material. In TABLE 4 data are also reported for the percent glucose, xylose and the remainder of the hydrolzyed material obtained by difference. Most of the samples prepared at 300-350°C show only minor amounts of hydrolyzed material except for samples MP-16, MP-13 and MP-14 prepared at low pressure or low flow rate. The percents of glucose and xylose for these samples as well as those for the samples prepared at 250°C are plotted on FIGURE 8. The rather well defined curve indicates that contrary to what was reported from the analysis of SCE oils (3) cellulose and hemicellulose are simultaneously degraded at or below 250°C.

The values for the percent in hydrolyzed material other than glucose or xylose (TABLE 4) are of special interest. They show that in samples prepared at 250°C up to 35% of the mass of initial dry wood is present in the residues as hydrolyzable products or


Solid residue
Recondensed material
○ H/C
□ O/C
H/C or O/C
2,0
1,6
1,2
0,8
0,4
0,0
250
275
300
325
350
250
275
300
325
350
Temperature, °C
(15)
(17)
(22)
(6)
(16)(13)
(18)
(20)(21)
(9)
(12)
(27)
(24)
(16)
(11)
(8)
(14)
(20)
(21)(9)

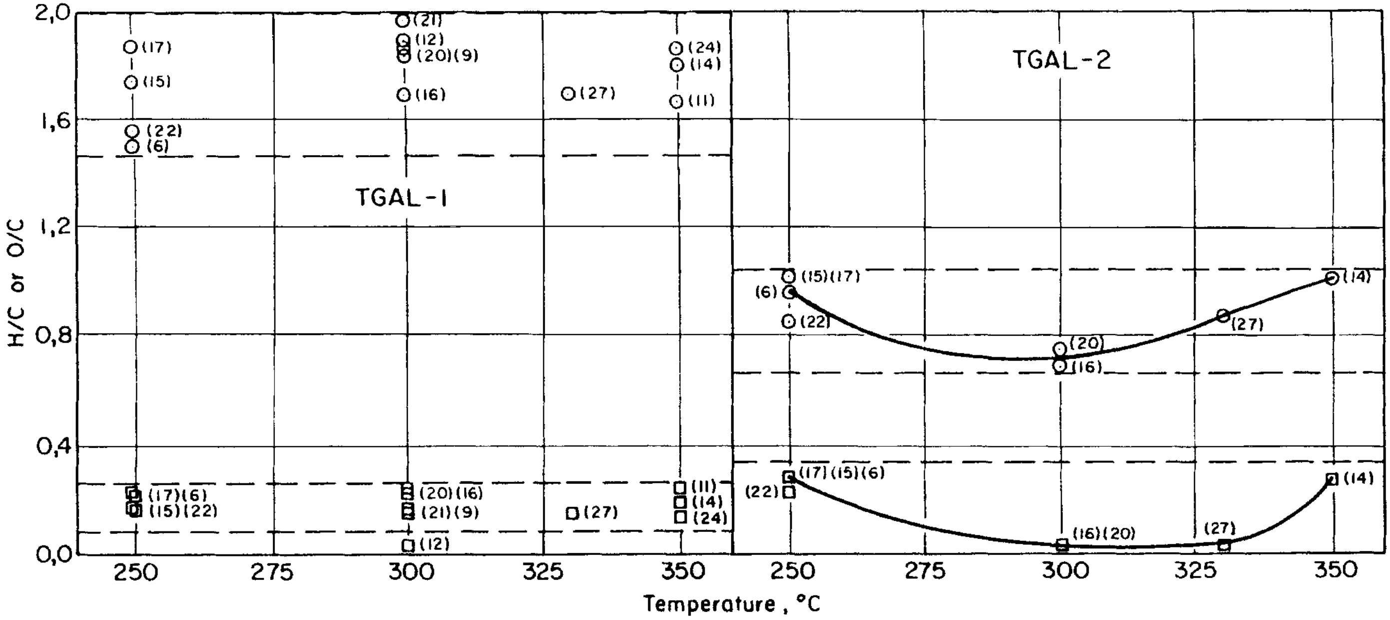


FIGURE 6. Elemental Analysis for SCE residues, TGAL-1 and -2 and recondensed material.

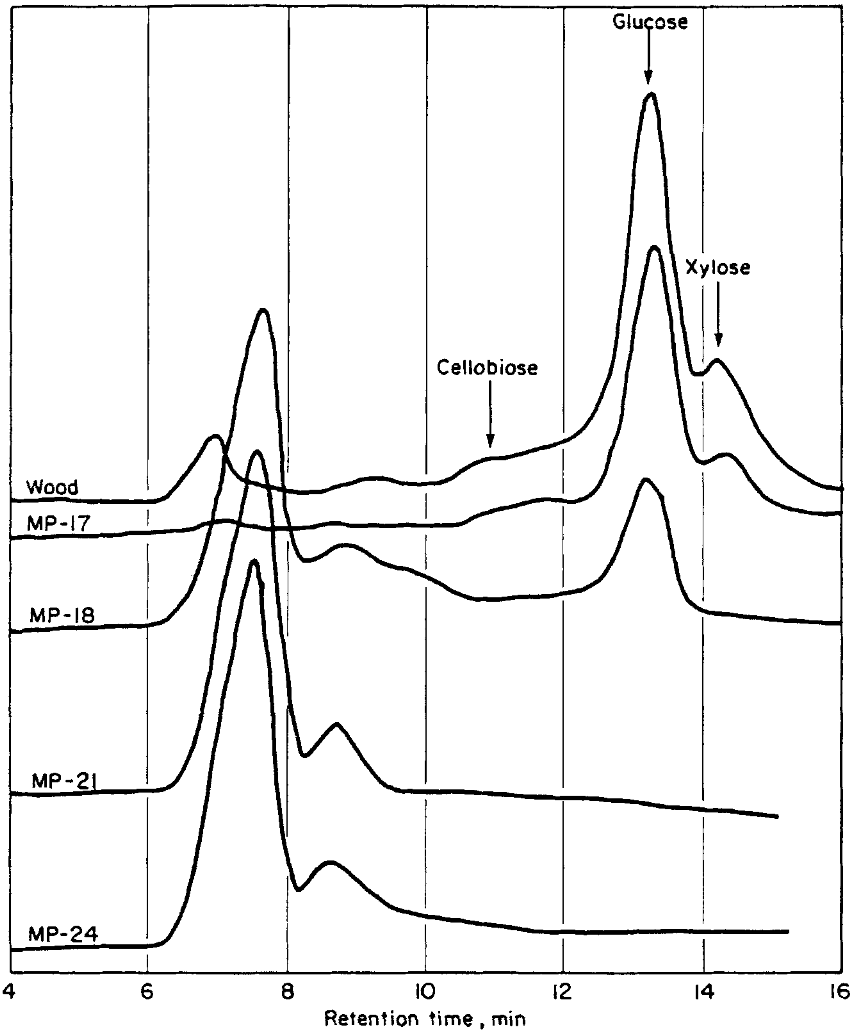


FIGURE 7. HPLC chromatograms of TFA hydrolyzates.

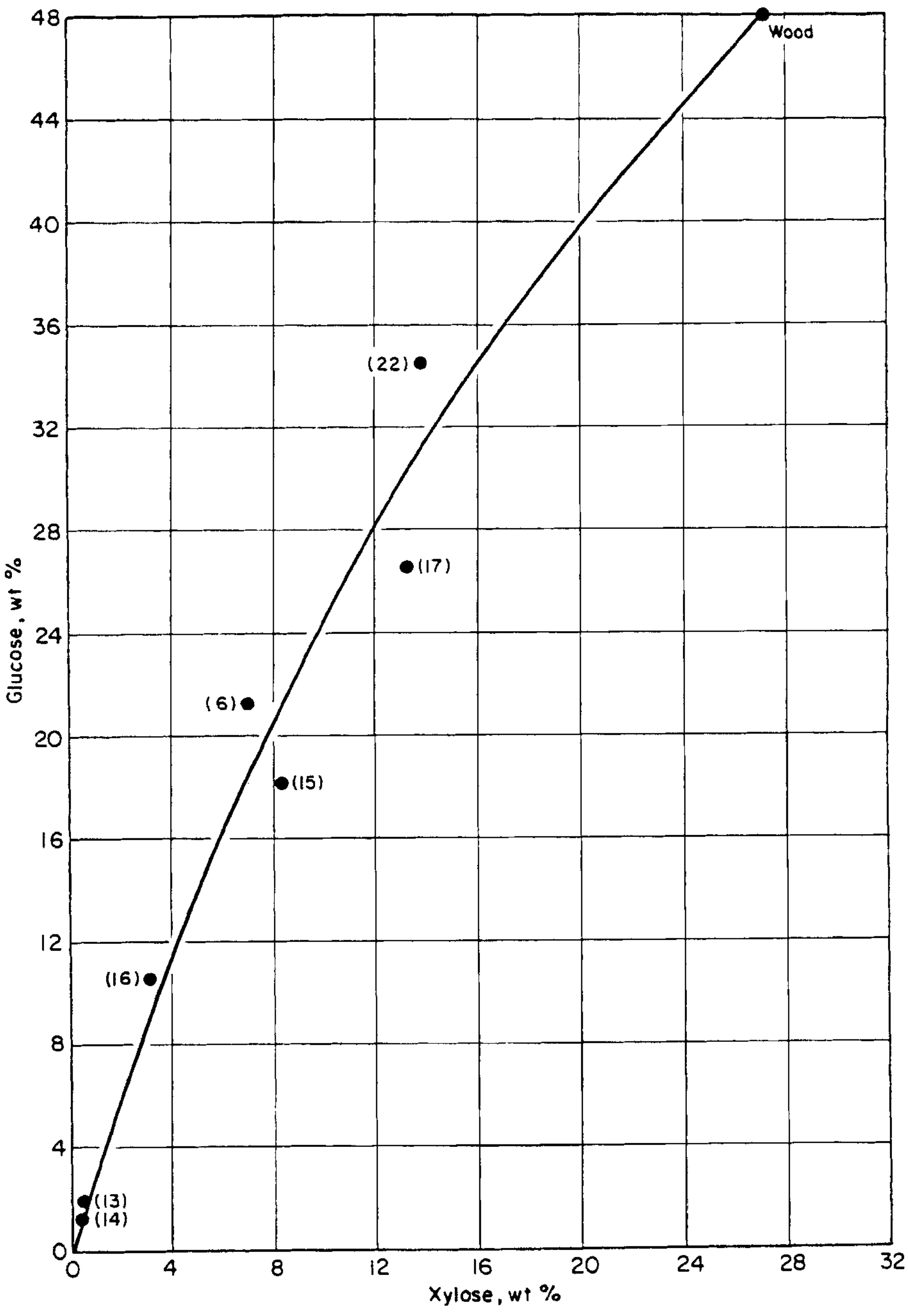


FIGURE 8. Residual hydrolyzed glucose as a function of residual hydrolyzed xylose.

carbohydrate conversion. The compound eluting at 7-8 min in the chromatogram of sample MP-24 (FIGURE 7) was isolated by evaporation and IR spectra of the white crystalline solid (KBr) shows strong bands at 1670, 1200 and 1140 cm^{-1} and medium intensity bands at 3400, 1460, 845, 800 and 720 cm^{-1}. This spectrum indicates a non-carbohydrate compound (absence of bands at 1000-1100 cm^{-1}). The bands at 720, 800 and 845 cm^{-1} suggest a furan-like structure and those at 1670, 1200 and 1140 cm^{-1} correspond to a TFA acid derivative.

CONCLUSION

The various results reported in this paper suggest a systematic procedure for the characterization of thermally degraded wood samples. This procedure would include a TFA test which is equivalent to a Klason test, and a thioglycolic acid test.

The thioglycolic acid test yields a determination of non-converted lignin (NCL), whereas the solid residue of the TFA test gives an estimation of the sum of non-converted lignin and recondensed material (NCL + RM). This RM fraction although constituted of recondensed lignin contains also material derived from carbyhydrates.

The liquid fraction collected during the TFA test may be analyzed for hydrolyzed glucose (HG) and xylose (HX) which may considered as a rough representation of unconverted cellulose and hemicellulose respectively.

The remaining material present in the TFA soluble fraction is to be considered as indicative of an acid soluble converted carbohydrate fraction (ASCC).

The five parameters NCL, RM, HG, HX and ASCC would thus provide a rather simple realistic characterization of any thermally degraded wood sample.

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