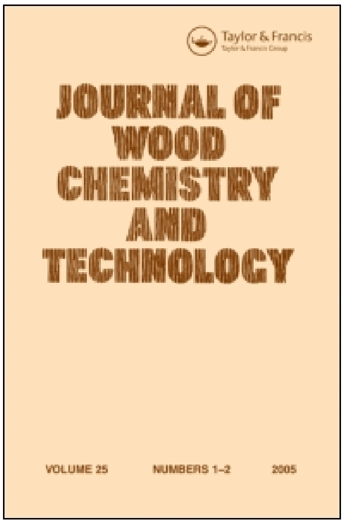

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Chemicals Generated During Oxygen-Organosolv Pulping of Wood

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CHEMICALS GENERATED DURING OXYGEN-ORGANOSOLV PULPING OF WOOD

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ABSTRACT

In this paper, we have characterized the black liquors from oxygen-organosolv pulping of *Eucalyptus globulus* wood in ethanol/water solutions (50:50, V/V) and acetic acid/water solutions (80:20, V/V).

After pulp separation, the organic solvent has been distilled and recycled; the precipitated lignin has been recovered by filtration. The degradation products in solution have been easily separated by simple extraction techniques. Five main groups of compounds have been isolated: solid lignin (11-12% o.d.w.), sugars (10-17% o.d.w.), aliphatic acids (12,5%), aromatic acids (2% o.d.w.) and low molecular weight phenols (1% o.d.w.). Most of these compounds were identified by HPLC and GC. Solid lignins have been analyzed by FTIR and ^{13}C NMR spectroscopy.

It has been concluded that oxygen-organosolv pulping process can be a new and interesting way for pulp preparation with little pollution and possibility of total biomass recovery; alternatively, it can be used for the fractionation and valorization of the components of lignocellulosics, including agriculture residues.

INTRODUCTION

Wood is composed mainly of cellulose (45-60%), hemicelluloses (15-30%) and lignin (20-30%). In classical chemical pulping methods, only 45% of the initial wood is recovered as cellulosic pulp. Dissolved polysaccharides, lignin and its degradation products, are generally used for their fuel value, after black liquor concentration.

Organosolv pulping processes allow total recovery and valorization of the biomass used for the production of cellulose fibres [1]. After the cooking operation and separation of pulp obtained, from the black liquor, the organic solvent is distilled and can be used in a new pulping cycle or in washing operation. Extracted lignin precipitates and is then isolated by filtration or centrifugation. The degradation products in the aqueous phase can be separated by simple extraction techniques. All these by-products can find interesting industrial applications [1].

However, most of the organosolv pulping processes make use of inorganic catalysts [2,3]. The presence of these can disturb the process of recovery of the pulping by-products. A new organosolv pulping method which uses molecular oxygen, without any mineral catalyst - the oxygen-organosolv process - has been recently developed [4-10]. The pulps are very well delignified (>90%), with high yields (>50%)[4-10], and the pulping by-products can be totally and easily recovered and separated [11,12].

This paper deals with the fractionation and characterization of the components of the black liquors, including extracted lignin, from oxygen-organosolv pulping of *Eucalyptus globulus* wood in ethanol/water and acetic acid/water media. The analysis of the solid polysaccharides fraction (cellulose fibres) has been previously reported[13].

MATERIALS AND METHODS

Wood Charateristics

We have used industrial chips of *Eucalyptus globulus* wood grown in Portugal (8-12 years old). The chemical composition (in % o.d.w) is the following: cellulose: 57.9%, lignin: 24.4%, pentosan: 19.1%, extractives (water+dichloromethane): 4.6%.

TABLE 1

Pulping Conditions and Results.

		$EtOH/H_2O$	$EtOH/H_2O/O_2$	$AcOH/H_2O/O_2$
Pulping Conditions	Temperature, °C	160	160	150
	Time to temp., min	90	90	90
	Cooking time, h	4	2	2
	Liquor-to-wood ratio	10	10	10
	pO_2, bar (25°C)	-	15	15
Pulping Results	Kappa number	61	17.5	25.6
	Delignification, %	74	93.8	91.8
	Pulp yield, %	59	49.9	51.3

Pulping Conditions and Results

The detailed conditions and results from oxygen-organosolv pulping of *Eucayptus globulus* wood in ethanol/water and acetic acid/water media can be found in our previous reports [8,9]; we have chosen two optimized oxygen-organosolv cooking experiments, referred respectively as $EtOH/H_2O/O_2$ and $AcOH/H_2O/O_2$, which we have used in this work. A cooking experiment in ethanol/water medium without oxygen, referred as $EtOH/H_2O$, was carried out to extract lignin which has been used as reference for lignin analysis. Pulping conditions and results of these three cooking experiments are summarized in TABLE 1.

Fractionation of the Black Liquor Components

After dilution of the black liquor with water (to avoid the formation of sticky lignin agglomerates) (FIGURE 1), the solvent has been distilled under vacuum at

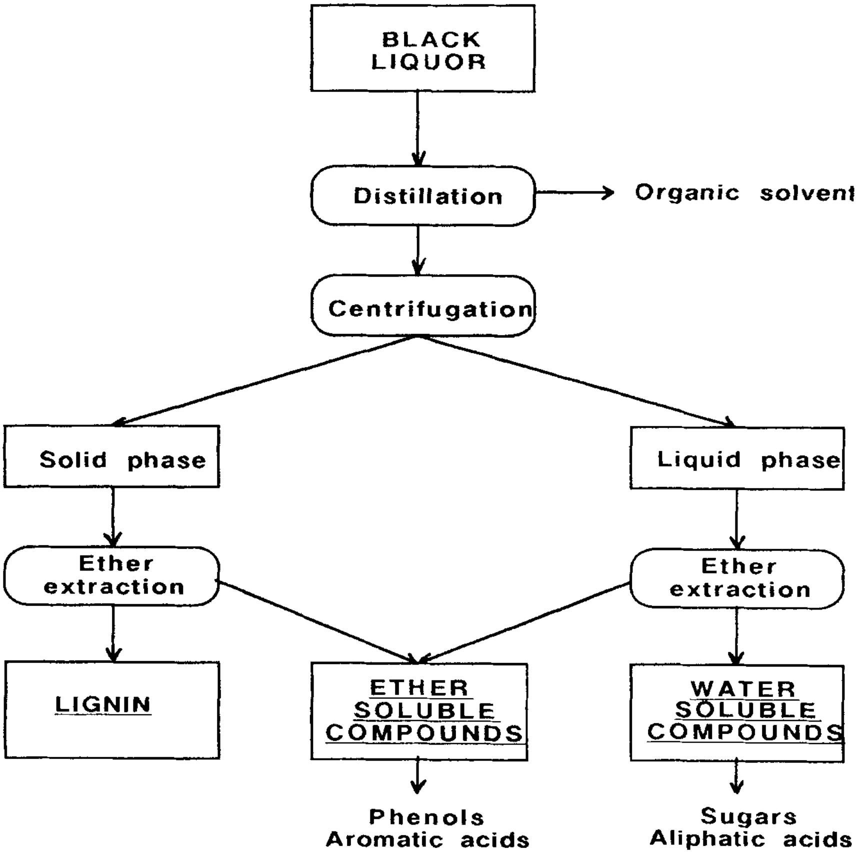


FIGURE 1. Black Liquor Fractionation Scheme

50 °C. The precipitated lignin has been recovered by centrifugation. Lignin derived low molecular weight compounds have been extracted with ether from solid lignin and from the aqueous solution. Three fractions have been obtained: lignin, ether soluble compounds and water soluble compounds (FIGURE 1).

The ether soluble compounds have been further separated into aromatic acids by the extraction with $NaHCO_3$ 5% aqueous solution, and phenols, by extraction with NaOH 5% solution. After acidification of the alkaline solutions to pH 1-2, these compounds have been extracted again with ether and recovered as solids, after evaporation of the solvent. The remaining ether soluble compounds in the initial ether extract have been designated as neutral compounds.

The water soluble compounds have been separated into aliphatic acids and sugars, by treatment of the aqueous solution with an anion exchanger resin (Amberlite IRA-93). Sugars have been recovered in solid form after water evaporation under vacuum at 50 °C. The acids retained by the resin have been recovered with 6M formic acid aqueous solution. After distillation of water and formic acid, the non-volatile aliphatic acids fraction have been obtained in the solid form. Volatile acids (for $EtOH/H_2O/O_2$ cookings) have been obtained by steam distillation of the black liquor.

Analysis of the Water Soluble Compounds

Sugars and aliphatic acids have been dissolved in water and analyzed by HPLC. For sugars the analysis conditions have been the following:

- Column: Polyspher OAHY (Merck);
- Temperature: 35 °C;
- Elution: H_2SO_4 0.01 N, 0.8 ml/min.

For aliphatic acids the conditions have been the following:

- Column: Polyspher CH PB (Merck);
- Temperature: 80 °C
- Elution, H_2O, 0.4 ml.

For both HPLC experiments, detection has been made by differential refractometry.

Analysis of the Ether Soluble Compounds

Aromatic acids have been analyzed as trimethylsilyl derivatives dissolved in dioxane, using Gas Chromatography (GC) and 4-hydroxy phtalic acid as an internal standard. The silyl derivatives have been prepared according to Pelizzari et al [14].The conditions used for GC have been the following:

- Column: SE 52;
- Temperature program: 4 min at 135 °C, gradient to 250 °C (6 °C/min), 10 min at 250 °C;
- Injector temperature: 250 °C;
- Detector temperature: 280 °C (FID).

Phenols dissolved in ethanol have been analyzed by GC and dibuthylphthalate has been used as an internal standard. The conditions used have been the same as for the trimethylsilyl derivatives of the aromatic acids, except for the temperature program which has been the following: 4 min at 115 °C, gradient to 240 °C (6 °C/min), 10 min at 240 °C.

Analysis of Lignin

Elemental analysis has been performed at the laboratories of the Service Central d'Analyse of CNRS (Vernaison, France). The oxygen content was calculated by subtraction of the sum of carbon and hydrogen from 100%.

The alkoxyl groups have been determinated by the Zeisel method modified by Girardin and Metche [15]. Alkoxyl groups have been converted to the corresponding alkyl iodides by reaction with iodic acid. The alkyl iodides in benzene solution have been analyzed by GC under the following conditions, using hexane as an internal standard :

- Column: Carbowax 20 M / silanised Chromosorb (80-100 mesh);
- Column temperature: 80 °C
- Injector temperature: 45 °C;
- Detector temperature: 50 °C (FID).

The calibration curves for methoxyl and ethoxyl groups have been constructed by means of standard solutions of methyl iodide and ethyl iodide, obtained respectively from vanillic acid and ethyl vanillin solutions treated with iodic acid.

Total number of $\rangle C{=}O$ groups has been determined by reaction of lignin with hydroxylamine hydrochloride in the presence of triethanolamine (TEA).

Liberated hydrochloric acid reacts with TEA and the excess of TEA is titrated with a standard solution of HCl. The details can be found elsewhere [10,16].

Infrared spectra have been recorded on a FTIR Bruker IFS 45 instrument. ^{13}C NMR spectra of DMSO-d$_6$ lignin solutions have been recorded by Danielle Robert (CENG, Grenoble, France) on a Bruker WM 250 instrument (^{13}C Frequency=62.8 MHz, T=323° K, Internal Reference: TMS).

RESULTS AND DISCUSSION

Material Balance

The material balance for EtOH/H_2O/O_2 and AcOH/H_2O/O_2 processes is summarized in TABLE 2.

In spite of the different sources of error associated with the different fractionation operations of the components of the black liquors, results of TABLE 2 indicate clearly that the oxygen-organosolv process can be an interesting approach to the complete recovery and valorization of the biomass components in wood pulping industry.

For the two solvent systems, from 100 g of wood we can obtain about 50 g of nearly pure cellulose pulp, 11-12 g of solid lignin, 10-17 g of sugars, nearly 12.5 g of aliphatic acids, 1.2 g of phenols and 1.9-2.4 g of aromatic acids.

Only about 50 % of the total extracted lignin has been recovered in the solid form, which means that a large lignin fraction is dissolved into low molecular weight compounds. This is due to extensive acid catalyzed hydrolysis and oxidation reactions. Unfortunately, only a small fraction of this dissolved lignin has been recovered as phenol compounds and aromatic acids. This fact can be assigned probably to condensation reactions which have taken place during acidification of the alkaline aqueous extracts (see experimental details) of these compounds, leading to precipitation and to the loss of this fraction in the subsequent ether extraction.

TABLE 2. Material Balance for $EtOH/H_2O/O_2$ and $AcOH/H_2O/O_2$ processes.
(results in % o.d.w.)

	$EtOH/H_2O/O_2$	$AcOH/H_2O/O_2$
PULP		
Holocellulose	48.4	49.3
Residual lignin	1.5	2.0
EXTRACTED LIGNIN		
Recovered solid lignin	12.3	11.2
Dissolved lignin *	10.6	11.2
WATER SOLUBLE COMPOUNDS		
Sugars	17.0	10.1
Non volatile acids	9.8	7.8
Volatile acids	2.7	-
ETHER SOLUBLE COMPOUNDS		
Phenols	1.2	1.2
Aromatic acids	1.9	2.4
Neutral compounds	0.3	0.1
CO_2 formed	3.3	3.6
O_2 consumed	8.9	9.1
TOTAL**	96.7	-

* Obtained by subtraction of the water insoluble lignin from the initial lignin content of wood; ** Obtained by subtraction of % O_2 consumed from the sum of all products formed (except ether soluble compounds).

Water Soluble Compounds

A great amount of polysaccharides dissolved during delignification reactions can be recovered as sugar monomers or oligomers (TABLE 2), depending on the solvent nature: 10 %/o.d.w. for $AcOH/H_2O/O_2$ and 17 %/o.d.w. for $EtOH/H_2O/O_2$ cooking, corresponding to about 40 and 70 % respectively of the total

TABLE 3. Sugars Identified in Oxygen-Organosolv Black Liquors.

SUGARS	$EtOH/H_2O/O_2$		$AcOH/H_2O/O_2$	
	% / total sugar recov.	% / o.d.w.	% / total sugar recov.	% / o.d.w.
Glucose	3.9	0.7	4.0	0.4
Xylose	22.4	3.8	30.4	3.1
Galactose	9.8	1.7	6.9	0.7
Arabinose	2.2	0.4	2.8	0.3
Mannose	1.4	0.2	16.9	1.7
Total identified, %	39.7		61.0	

polysaccharides dissolved. This result is extremely interesting because due to the acidic and oxidative conditions of the pulping system, significant degradation of the dissolved sugars would be expected.

About 40 and 60 % of the sugars fraction recovered from $EtOH/H_2O/O_2$ and $AcOH/H_2O/O_2$ black liquors respectively have been identified as monomers (TABLE 3).

The main sugars identified are xylose, galactose and mannose, indicating an extensive hydrolysis of the hemicelluloses during pulping reactions. Glucose is found only in minor amounts. The composition of the sugar fraction is also very different for the two solvents indicating a different behaviour of the hemicelluloses during pulping reactions and/or different stabilities of the monomers in the two organic solvent media.

Concerning the analysis of the aliphatic acids fraction, results have been obtained only for the $EtOH/H_2O/O_2$ cooking (TABLE 4).

About 70 % of the aliphatic acids recovered have been identified. These acids are mainly pyruvic, oxalic, acetic and formic acids. They come essentially from oxidation reactions of lignin and sugars [8,9].

TABLE 4. Aliphatic Acids Identified in $EtOH/H_2O/O_2$ Black Liquors.

ALIPHATIC ACIDS	% / total aliphatic acids recovered	% / o.d.w.
Oxalic	15.2	1.9
Pyruvic	32.0	4.0
Glycolic	traces	traces
Gyceric	traces	traces
Formic	11.2	1.4
Acetic	10.4	1.3
Total identified, %	68.9	

Ether Soluble Compounds

Low molecular weight phenols extracted by ether, represent about 1.2 % / o.d.w. for the two organic solvent media considered (TABLE 2). About 70 % of the recovered phenols in $AcOH/H_2O/O_2$ cooking have been identified, against only about 30% in $EtOH/H_2O/O_2$ cooking (TABLE 5). Reactions of the organic solvent with lignin, particularly ethylation of some phenolic hydroxyl groups, could account for this observation.

The main compounds identified are syringaldehyde, syringol and vanillin, products of the extensive oxidation and hydrolysis of lignin. Although, their relative abundance is different for the two organic solvent media, indicating that relatively different delignification mechanisms can take place in the two solvent media.

The aromatic acids fraction represents about 1.9 %/o.d.w. in $EtOH/H_2O/O_2$ and 2.4 % /o.d.w. in $AcOH/H_2O/O_2$ cooking (TABLE 2). Only 30 % and 40 % respectively of the total recovered aromatic acids have been identified (TABLE 6).

The main compounds identified are 4-hydroxybenzoic acid and syringic acid. The presence of these compounds in relatively significant amounts confirms the extensive oxidation of lignin.

TABLE 5. Phenols Identified in Oxygen-Organosolv Black Liquors.

PHENOLS	$EtOH/H_2O/O_2$		$AcOH/H_2O/O_2$	
	% / total phenols recovered	% / o.d.w.	% / total phenols recovered	% / o.d.w.
Vanillic alcohol	0.1	traces	0.5	0.07
Vanillin	8.6	0.10	14.1	0.17
Syringol	5.0	0.06	37.6	0.46
Syringaldehyde	16.4	0.20	14.6	0.18
Acetosyringone	2.4	0.03	2.2	0.03
Total identified, %	32.5		69.0	

TABLE 6. Aromatic acids Identified in Oxygen-Organosolv Black Liquors.

AROMATIC ACIDS	$EtOH/H_2O/O_2$		$AcOH/H_2O/O_2$	
	% / total arom. acids recovered	% / o.d.w.	% / total arom. acids recovered	% / o.d.w.
4-Hydroxybenzoic	12.0	0.22	6.8	0.16
Syringic	12.3	0.23	25.3	0.61
3,4,5-Hydroxybenzoic	0.9	0.02	1.7	0.04
Phtalic	4.3	0.08	6.2	0.15
Isophtalic	0.4	0.01	0.6	0.01
Total identified, %	29.9		40.6	

TABLE 7. Chemical Analysis of Organosolv and Oxygen-Organosolv Lignins (results in % / o.d.lignin).

	$EtOH/H_2O$	$EtOH/H_2O/O_2$	$AcOH/H_2O/O_2$
Elemental Analysis:			
C	60.0	57.6	56.9
O	34.4	36.9	38.1
H	5.6	5.5	5.0
Methoxyl	19.5	16.0	16.1
Ethoxyl	1.4	5.7	-
Total $\gt C{=}O$	2.2	5.7	7.7

Lignin

The results of the chemical analysis of the extracted lignins are summarised in TABLE 7.

The elemental composition of the three lignins is not significantly different. However, the oxygen content is somewhat higher for oxygen-organosolv lignins because of the oxidation reactions which induce the formation of relatively high amounts of $\gt C{=}O$ groups (TABLE 7): 5.7 and 7.7 % (o.d.lignin) for oxygen-organosolv lignins against only 2.2 % (o.d.lignin) for organosolv ($EtOH/H_2O$) lignin. Methoxyl content is also lower for oxygen-organosolv lignins, indicating that in the presence of oxygen the elimination of this functional group takes place. Lignins obtained in ethanol/water medium also contain a high content of ethoxyl groups confirming that reactions between the organic solvent and lignin have taken place. In the presence of oxygen ($EtOH/H_2O/O_2$ cooking), ethylation is particularly important.

Infrared spectra of organosolv ($EtOH/H_2O$) (FIGURE 2) and oxygen-organosolv ($EtOH/H_2O/O_2$ and $AcOH/H_2O/O_2$) lignins (FIGURE 3) are not very different, except for the 1650-1730 cm^{-1} spectral region.

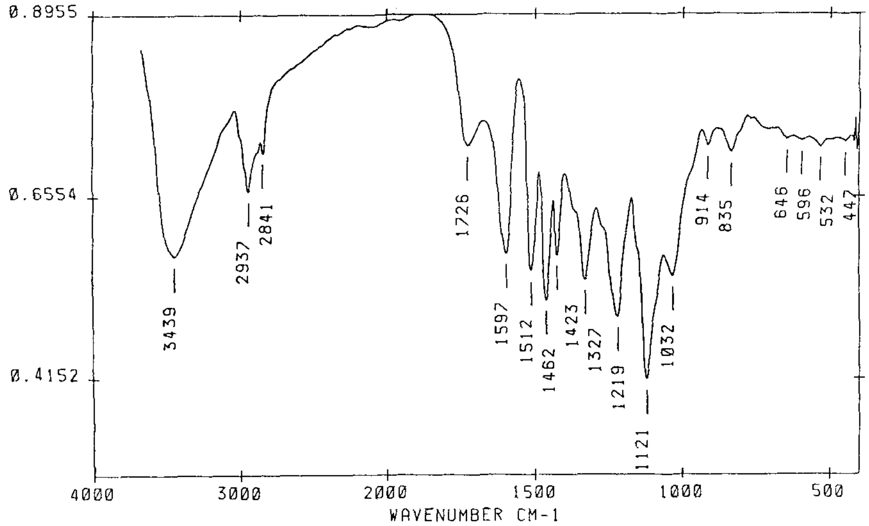


FIGURE 2. FT/IR Spectrum of Organosolv ($EtOH/H_2O$) Lignin .

A strong absorption band at 1725-1730 cm^{-1} confirms the presence of relatively high amounts of non-conjugated $>$C=O groups in $EtOH/H_2O/O_2$ and $AcOH/H_2O/O_2$ lignins. An absorption band at 1660 cm^{-1} indicates also the presence of $>$C=O groups conjugated with the aromatic ring, particularly in $EtOH/H_2O/O_2$ lignins.

The 1725-1730 cm^{-1} absorption band is stronger for $AcOH/H_2O/O_2$ lignin than for $EtOH/H_2O/O_2$ lignin. This is probably due to some acetylation in the former. To confirm this, we have dissolved and saponified the $AcOH/H_2O/O_2$ lignins with 0.5 M NaOH aqueous solution, liberating the acetyl groups, followed by lignin re-precipitation with aqueous HCl to a pH of 1-1.5. This treatment has led to a decrease of the 1725-1730 cm^{-1} absorption band, confirming the the partial acetylation of $AcOH/H_2O/O_2$ lignins and the higher $>$C=O content found by chemical analysis.

FIGURE 4 represents ^{13}C NMR spectra of oxygen-organosolv lignins; signal assignments [17] are summarized in TABLE 8. ^{13}C NMR spectrum of

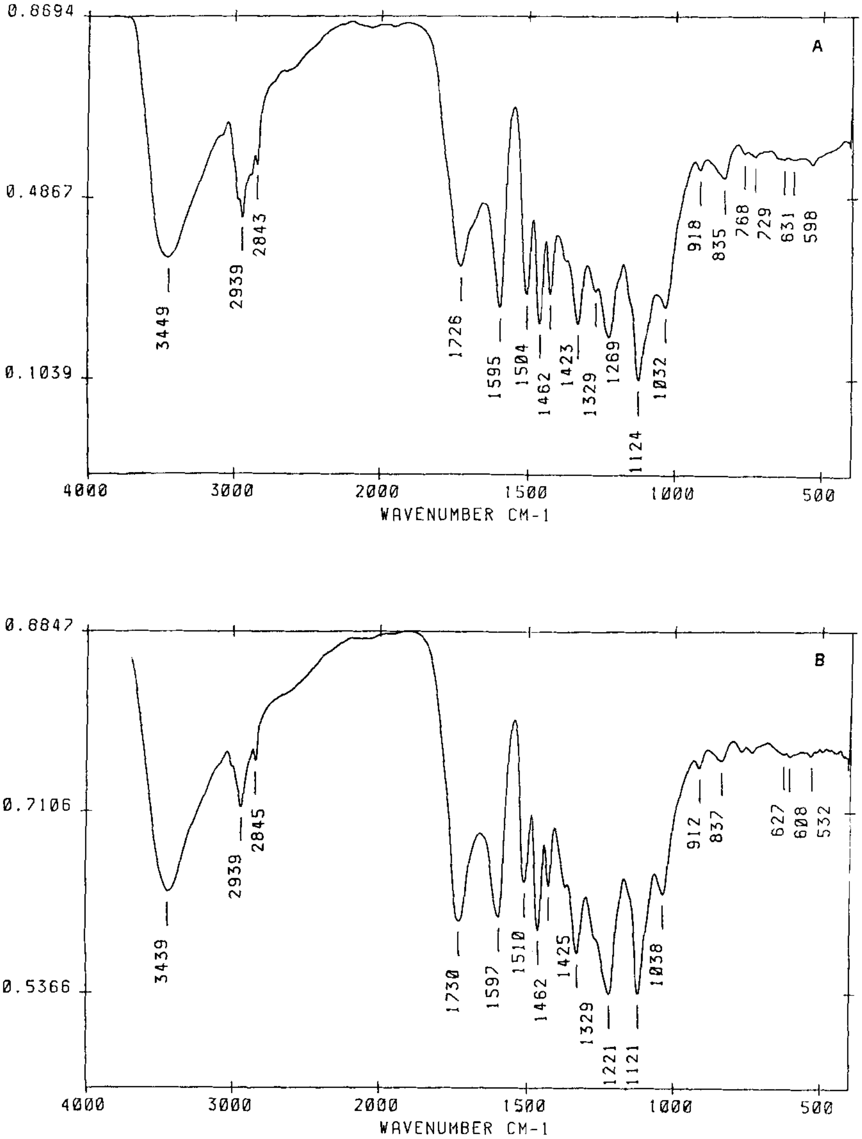
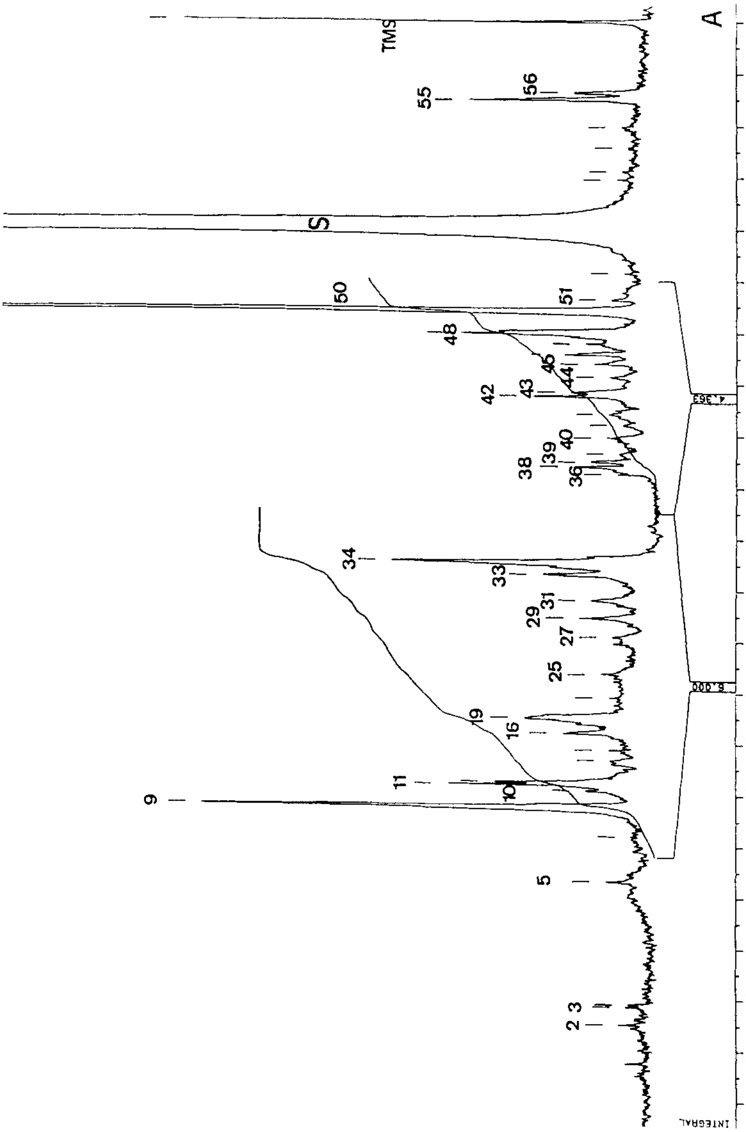


FIGURE 3. FT/IR Spectra of Oxygen-Organosolv Lignins. A: EtOH/H_2O/O_2 Lignin; B: AcOH/H_2O/O_2 Lignin.

TABLE 8. ^{13}C Chemical Shifts and Signal Assignments for Oxygen-Organosolv Lignins.

Signal number	δ, ppm/TMS	Assignments*
2	194.9	-CHO in cinnamaldehyde units
3	191.5	α -CHO in benzaldehyde units
4	171-173	-C=O in ester units
5	165-167	-C=O in Ar-COOH units
9	152.2	C-3/C-5 in S e
10	149.2	C-3 in G e
11	148.0	C-4 in G e
16	138.0	C-1 in S β-O-4 e
19	135.0	C-4 in G and S
25	126.5	C-β in cinnamaldehyde units
27	119.2	C-6 in G e and ne
29	115.4	C-5 in G e and ne
31	112.0	C-2 in G
33	107.3	C-2/C-6 in S with α C=O or α C=C
34	105.6	C-2/C-6 in S
35	104.3	C-2/C-6 in β-β units
36	87.4	C-β in S β-O-4 threo
38	85.9	C-β in S β-O-4 erythro
39	85.0	C-α in β-β units
40	80.4	C-α in G and S β-O-4/α-O-4 units
42	72.4	C-α
43	71.6	C-γ in β-β units
44	68.6	$-CH_2$ in $-OCH_2CH_3$ units
45	66.0	$-CH_2$ in $-OCH_2CH_3$ units
48	60.2	C-γ in G and S β-O-4 units
50	55.9	$-OCH_3$
51	53.7	C-β in β-β units
55	15.2	$-CH_3$ in $-OCH_2CH_3$ units
56	13.7	$-CH_3$ in $-OCH_2CH_3$ units

*S: syringyl unit, G: guaiacyl unit, e: etherified unit in C-4, ne: non etherified unit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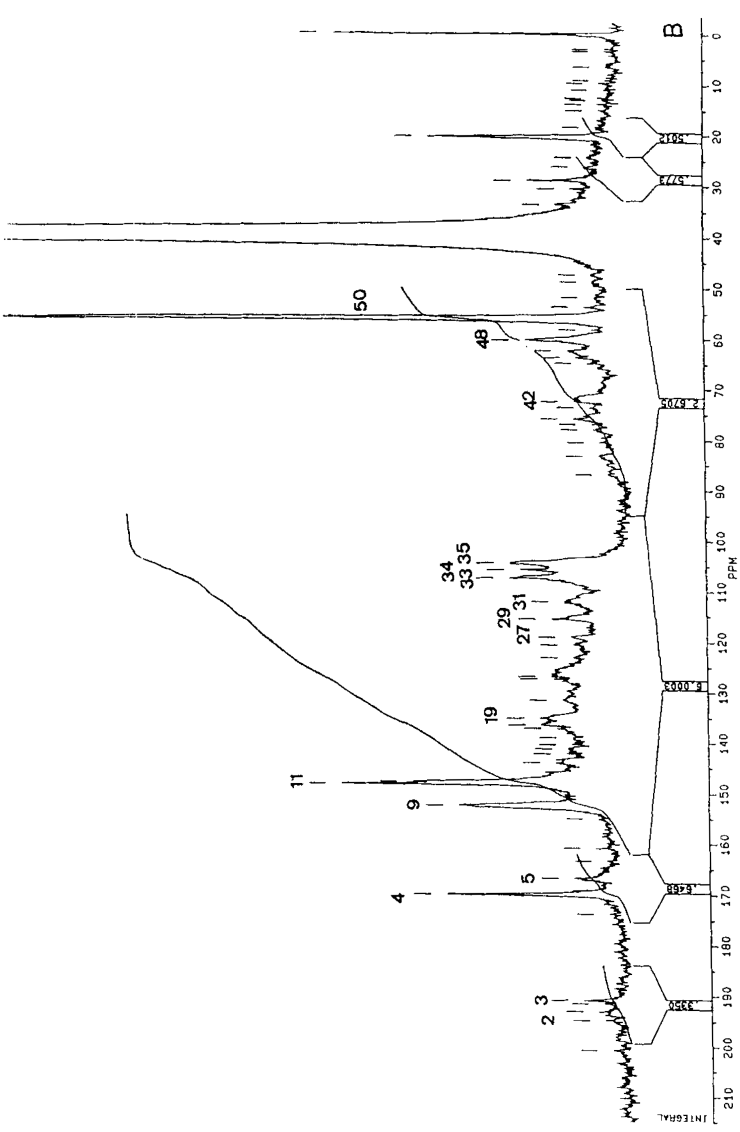

FIGURE 4. ^{13}C NMR Spectra of Oxygen-Organosolv Lignins. A: EtOH/H_2O/O_2 Lignin; B: AcOH/H_2O/O_2 Lignin.

$EtOH/H_2O/O_2$ lignin (FIGURE 4.A.) indicate that the structure of lignin obtained from oxygen-organosolv pulping in ethanol-water medium is similar to that of organosolv ($EtOH/H_2O$) lignin [10] and is not very different from that of typical MWL hardwood lignins [17]. This is a surprising result since important structural modifications would be expected, because of the relatively severe pulping conditions. On the contrary, $AcOH/H_2O/O_2$ lignin (FIGURE 4.B.) present very important structural modifications ; this can be partially assigned to association and recondensation reactions which could take place during pulping or during the reprecipitation and recovery operations, induced by the acidity.

The most important modification seems to be the introduction of $>C=O$ groups (signals at 166.8, 191.5 and 194.9 ppm) and functional groups arising from reactions of the organic solvent with lignin. Ethoxylation of $EtOH/H_2O$ and $EtOH/H_2O/O_2$ lignins is confirmed by ethoxyl $-CH_2$ goups at 63 and 65 ppm (FIGURE 4.A.). The use of the DEPT sequence [17], which evidences aliphatic carbons, has confirmed this result [10]. A signal at *c.a* 171 ppm confirms the partial acetylation of $AcOH/H_2O/O_2$ lignins (FIGURE 4.B.).

For more details, a specific paper dealing with ^{13}C NMR spectra of organosolv and oxygen-organosolv lignins has been recently presented [18].

CONCLUSIONS

The black liquor components of oxygen-organoslv pulping process can be completely separated by simple extraction and separation techniques leading to relatively well defined families of chemical compounds. These include lignin, sugars (monomers and oligomers), aliphatic acids, phenols and aromatic acids.

These compounds may be used as important raw materials for chemical industries. Due to their high number of $>C=O$ groups, oxygen-organosolv lignins can be used in the synthesis of polymers, such as polyamides, in addition to the classical uses of the common technical lignins. Xylose, the main component of the sugars fraction, can find several applications including the production of furfural and furan based compounds . The whole sugar fraction can be alternatively used for the production of ethanol; this ethanol could be used to compensate eventual organic solvent losses in the $EtOH/H_2O/O_2$ process. The aliphatic acids fraction can be utilized directly in several chemical industries. The low molecular weight phenol derivatives fraction which is composed mainly of vanillin, vanillic alcohol, syringic acid and 4-hydroxybenzoic acid may also find interesting applications in industrial organic synthesis.

These results show that the oxygen-organosolv technique may be a new alternative pulping process, allowing a complete recovery of all the products formed during delignification reactions and leading to a more extensive use of the whole wood biomass. Alternatively it can constitute an interesting method for the fractionation and valorization of forest products or other lignocellulosic materials such as agricultural residues or residual products from the agro-food industries.

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