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Singlet oxygen degradation of lignin in the pulp

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Abstract

The lignins obtained from steam explosion of straw and beech at log R_0 3.94 and 4.45 were characterised. Elemental analysis, gel permeation chromatography, UV, ^1H and ^{13}C NMR spectra allow defining the characteristics of the lignins used. Pulps obtained from the steam explosion process were used as starting materials. The amount of lignin in the pulps was determined by using the Klason lignin determination. The lignins in pulp were irradiated with a visible light in the presence of Rose Bengal and oxygen in water suspension for 24 h. Extensive degradation of the lignin in the pulps was observed. In fact, the amount of lignin in the pulps dropped from 22–24% to 3–7%. The pulps from beech seem to be more sensitive to the process than that from straw. The same result was obtained by using cardboard. The irradiation with visible light of cardboard in water suspension with Rose Bengal in the presence of oxygen induced the reduction of the amount of lignin from 24% to 13%. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently we found that some lignin models and lignins derived from steam-explosion can undergo several modifications when treated with singlet oxygen [1–3]. In particular, we have seen that singlet oxygen is able to induce degradation of lignin model compounds of both the core and side chain of both hardwood and softwood lignins. We have seen that these model compounds underwent a $\beta\text{-C-O}$ cleavage. Probably, this cleavage involves the oxidation of the phenoxy part of the molecule. When this process is used on lignins from steam explosion, lignins were extensively degraded as shown by GLC chromatograms and UV spectra of the samples.

These results can broaden the use of photochemical process in the treatment of pulp. In fact, until now, after the abolition of chlorine treatment of pulps, the degradation of lignin was performed by using hydrogen peroxide. The only process available utilizing a photochemical process requires both UV irradiation and hydrogen peroxide [4,5].

In this paper we want to show that the singlet oxygen degradation of lignins can be a potentially useful method in the bleaching processes.

2. Materials and methods

^1H and ^{13}C NMR spectra were recorded with a Bruker 300 AM instrument. All the ^{13}C NMR spectra were recorded in $\text{DMSO-}d_6$. ^1H NMR spectra were recorded in CDCl_3 . The lignin samples were acetylated (acetic anhydride and pyridine) before the use. Cary 2300 spectrophotometer was used for the UV spectra. 1:1 $\text{CH}_3\text{CN-EtOH}$ mixture was used as solvent. Gel permeation chromatography analyses were performed on a Varian HPLC by using H-P Plgel 5 μ column. The lignin samples were acetylated (acetic anhydride and pyridine) before the use. THF was used as mobile phase. Spectrophotometric grade THF was used and distilled (oven LiAlH_4) before the use. The chromatograms were obtained using an UV detector at 280 nm. The conversion from elution time to molecular weight was performed by using a calibration obtained by using polystyrene samples. Elemental analyses were obtained with a Carlo Erba Elemental Analyzer 1106.

2.1. Pulp from steam explosion

The material used as source of lignin (straw, beech, and pine) was mechanically reduced to pieces of about 1 cm of length and added with water to rise its initial content to the

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Table 1
Steam explosion parameters

Sample	Source	Time (min)	log R_0^a	Cellulose (g)	Cellulose (%)	Lignin (g)	Lignin (%)
1	Straw	10	4.45	12.87	46.82	5.420	19.72
2	Beech	10	3.94	13.59	50.9	2.730	10.20
3	Beech	10	4.45	8.53	51.8	2.990	18.16

$$^aR_0 = t \cdot \exp(T-100)/14.75.$$

value of 50%. Steam explosion runs were carried in a 10 l batch reactor, loading about 0.5 kg of material each cycle. Treatment conditions were ranged from 188°C to 230°C and from 3 to 10 min. The treatment condition together with the correspondent severity parameters, R_0 , is reported in Table 1 [8]. The raw material (100 g) was extracted two times with hot water (250–300 ml, 65±5°C) in order to eliminate sugars and hemicelluloses. The extraction of lignin from exploded materials has been carried out by 1.5% sodium hydroxide solution (250 ml) at 90°C in 15 min for two times. Lignin was precipitated at pH 2 with 20% H₂SO₄ when the solution was still warm, filtered, washed, and dried at 105°C. The amounts of isolated lignins is reported in Table 1.

2.2. Klason lignin

The material used (1 g, 40 mesh) was put into an extraction thimble. A cotton ball was put on the top of the thimble and the thimble was put into a Soxhlet extraction apparatus. 95% Ethanol (200 ml) was added and the extraction was carried out for 7 h. The liquid from the extraction flask was filtered through the thimble using a little ethanol to rinse the flask. The above described procedure was repeated using dichloromethane and, then, using a 1:2 95% ethanol–toluene mixture. The residue was transferred to a 50 ml beaker. Cold 72% H₂SO₄ (15 ml) was added. The mixture was stirred at 20°C for 2 h. The mixture was poured into a 1 l beaker and diluted with 560 ml water. The beaker was covered with a large watch glass and refluxed for 4 h maintaining a constant volume with water. The mixture was filtered through a fritted glass crucible. The residue was dried in an oven at 110°C overnight.

2.3. Reactions of pulp from steam explosion with singlet oxygen

A suspension of pulp (100 mg) in water (10 ml) containing 5×10^{-4} M Rose Bengal was irradiated in a Pyrex tube

surrounded by a Pyrex water-jacket connected to a Haake D9-G thermostat to maintain the temperature at 13.0±0.1°C. The Pyrex tube was dipped into a 1% (w/v) solution of NaNO₂ in order to cut-off the irradiation at 400 nm. The solution was saturated previously with bubbling oxygen for 1 h. The irradiation was performed by using a 50 W tungsten–halogen lamp. After 24 h the reaction mixture was filtered and the residue was dried in an oven at 110°C overnight.

2.4. Reaction of recycled paper with singlet oxygen

Recycled paper (100 mg) containing 25.6% lignin (Klason) was finely hashed and suspended in water (10 ml) and stirred for 24 h at room temperature. To this mixture Rose Bengal (3 mg) was added and the mixture was saturated with bubbling oxygen for 1 h. Then, the mixture was irradiated in a Pyrex tube surrounded by a Pyrex water-jacket connected to a Haake D9-G thermostat to maintain the temperature at 13.0±0.1°C. The Pyrex tube was dipped into a 1% (w/v) solution of NaNO₂ in order to cut-off the irradiation at 400 nm. The irradiation was performed by using a 50 W tungsten–halogen lamp. After 24 h the reaction mixture was filtered and the residue was dried in an oven at 110°C overnight.

3. Characterization of lignins from steam explosion

The results of elemental analyses are collected in Table 2. We analysed the presence of carbon and hydrogen in order to characterize the lignin, but also the presence of both nitrogen and sulphur as a marker of the presence of proteic materials in the lignin and sulphur as a marker of the presence of sulphonated lignins. The presence of sulphur in our samples was detected only in sample 1 from straw. The elemental analysis allows us to give the molecular weight of the lignins expressed in phenylpropanoid (C₉) units. The data are collected in Table 2.

The distribution of acetylated lignins considering their molecular weights was obtained by using gel permeation chromatography. The results are depicted in the Figs. 1–3. Most of the molecules of our samples show a molecular distribution in the range 100–100 000.

The UV spectra of our samples were recorded in DMF. We recorded also the differential spectra obtained carrying out the spectrum of the samples in 1 M NaOH vs the standard solution in DMF. These data allow us to give the

Table 2
Elemental analysis, empirical formula, and molecular weights (in C₉ units) of lignins from steam explosion

Sampl	Elemental analysis					Empirical formula				MW
	N	C	H	S	O	C	H	S	O	
1	1.17	47.04	4.81	4.49	42.49	9	11.04	0.32	6.11	SNNN227
2	–	61.45	6.08	–	32.41	9	10.67	–	3.56	176
3	–	59.60	5.20	–	35.20	9	9.42	–	3.98	181

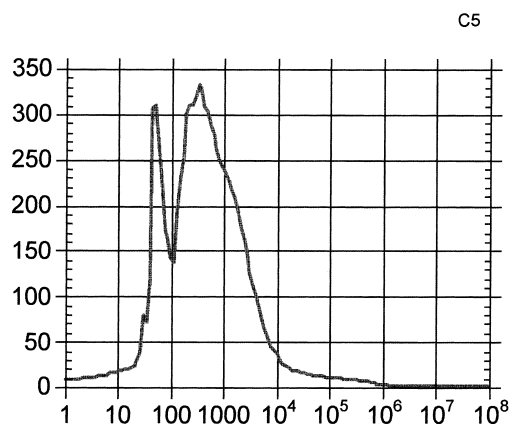


Fig. 1. MW distribution of lignin from straw (sample 1).

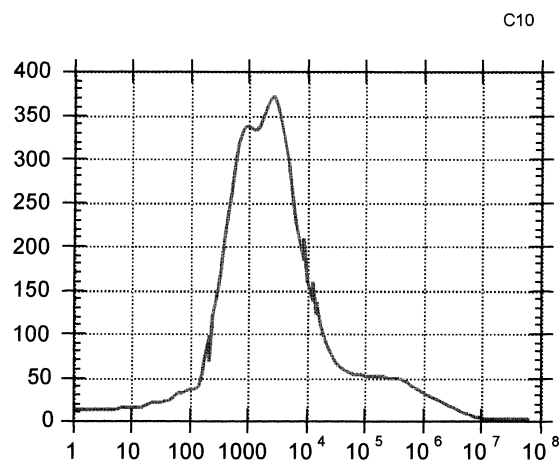


Fig. 3. MW distribution of lignin from beech (sample 3).

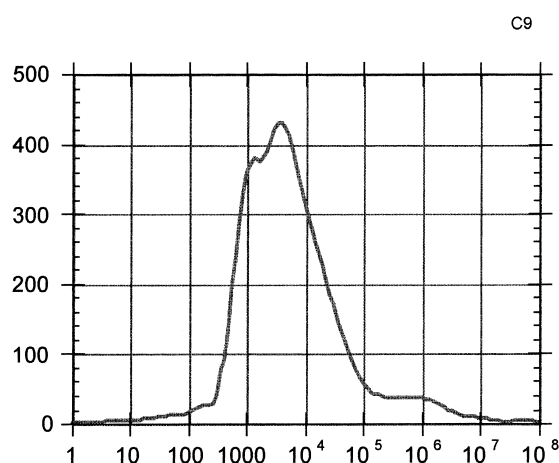


Fig. 2. MW distribution of lignin from beech (sample 2).

4. Results and discussion

In a previous paper [3] we reported that the irradiation at 600 nm of lignins from steam explosion in acetonitrile–ethanol in the presence of both Rose Bengal and oxygen led to an extensive degradation of the lignins. In order to broaden the potential usefulness of this method we tested the capability of singlet oxygen to induce lignin degradation in the pulp from steam explosion.

At this purpose, we used as source of lignins the beech (softwood lignin) and the straw. The amounts of lignin contained in the pulp was estimated determining the amount of Klason lignins in these samples. The Klason lignins were obtained by a severe treatment of the pulp with concentrated sulphuric acid. The results are reported in Fig. 4. The amount of lignin recovered in the samples fluctuated from 22% (beech) to 24% (straw).

The degradation of lignin in the pulp was carried out as follows: the pulp (100 mg) was suspended in water (50 ml) and saturated with oxygen. Rose Bengal was added and the mixture was irradiated under stirring with visible light for 24 h. The mixture was then filtered and the residue was dried in an oven at 110°C overnight. The degradation of the lignin was estimated on the basis of the loss of weight of the samples after this treatment. The results are reported in Fig. 4. The residual lignin in the sample varied from 9% (straw) to 5% (beech). Then, we can observe an evident degradation of the lignin in the pulp.

To confirm this datum we performed this type of test on cardboard. The amount of lignin was determined as

amount in mEq g^{-1} of some structural features in the lignin samples. In this case we were able to give the amounts of syringyl and guaiacyl phenols (Type I), the amounts of phenols containing conjugated double bonds (i.e. $\text{HO-Ar-CH=CH-CH}_2\text{OH}$, Type II), and the amounts of stilbenic phenols (Type IV). The results are reported in Table 3.

Finally, the characterization of the lignins used in this work was completed by using the ^1H and ^{13}C NMR spectroscopy. The signals observed with our samples are collected in Table 4.

The results obtained showed that the lignin in the sample treated showed the same properties of the lignin treated in a previous reported paper [3].

Table 3
UV spectra of lignins from steam explosion

Sample	λ_1 (nm)	D ($\text{l g}^{-1} \text{cm}^{-1}$)	λ_2 (nm)	D ($\text{l g}^{-1} \text{cm}^{-1}$)	λ_3 (nm)	D ($\text{l g}^{-1} \text{cm}^{-1}$)	Type I (meq g^{-1})	Type II (meq g^{-1})	Type IV (meq g^{-1})
1	324	8.80					0.20	–	0.06
2	277	17.60	308	10.20	340	6.40	2.47	0.29	0.14
3	274	24.60			340	11.40	0.85	0.13	0.08

Table 4
 ^1H and ^{13}C NMR spectra of lignins, δ ppm

Sample 1		Sample 2		Sample 3	
^1H NMR	^{13}C NMR	^1H NMR	^{13}C NMR	^1H NMR	^{13}C NMR
8.9	208	6.5–7	152	6.5–7	152
7.95	173	6	148	6	148
7.0	153	4.5	138	3.7	134
6.5	148	4.4	134	2.3	115
6.0	145	4.27	115	1.9–2.1	104.5
5.45	138	3.7	104.5	1.22	72
3.8	135.5	2.3	86	–	60
2.27	135	2	72	–	55
2.18	133	1.22	60	–	40
2.0	132	–	55	–	–
1.26	131	–	40	–	–
	126	–	–	–	–
	121	–	–	–	–
	120	–	–	–	–
	115	–	–	–	–
	112	–	–	–	–
	111	–	–	–	–
	107	–	–	–	–
	104.5	–	–	–	–
	79	–	–	–	–
	55.5	–	–	–	–
	28	–	–	–	–

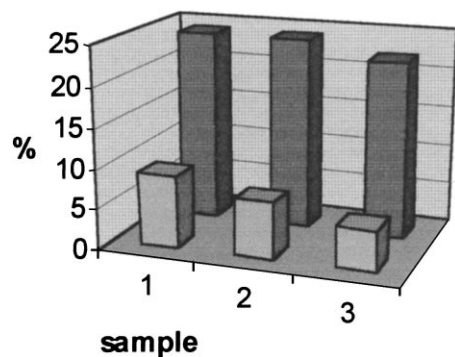


Fig. 4. Amount of klason lignin in the pulp from straw and beech (back) and the residual lignin after the treatment with singlet oxygen (in front).

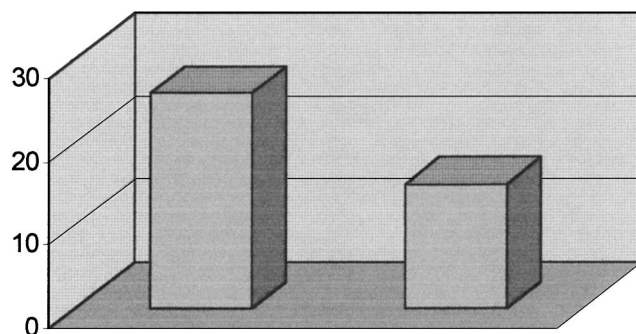


Fig. 5. Amount of klason lignin in the cardboard (left) and the residual lignin after the treatment with singlet oxygen (right).

Klason lignin as described before and the result was reported in Fig. 5. The cardboard was finely hashed and suspended in water. Rose Bengal was added and the mixture was irradiated with visible light in the presence of oxygen for 24 h. The loss of weight after the filtration was reported in Fig. 5 as residual lignin. We can see that more than half the lignin was degraded after the treatment with singlet oxygen.

Work is in progress devoted to use chemical generation of singlet oxygen.

References

- [1] C. Crestini, M. D'Auria, J. Photochem. Photobiol. A: Chem. 101 (1996) 69.
- [2] C. Crestini, M. D'Auria, Tetrahedron 53 (1997) 7877.
- [3] C. Bonini, M. D'Auria, L. D'Alessio, G. Mauriello, D. Tofani, D. Viggiano, F. Zimbardi, J. Photochem. Photobiol. A: Chem. 113 (1998) 119.
- [4] A. Castellán, Curr. Trends Polymer Photochem. 1 (1995) 211.
- [5] A.E.H. Machado, R. Ruggiero, M.G. Neumann, J. Photochem. Photobiol. A: Chem. 81 (1994) 107.