

Characterization of Photo-Yellowing Trigger Compounds Repressing Paper Recyclability

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The chemithermomechanical pulp (CTMP) papers prepared from different *Eucalyptus globulus* trees individuals, which showed various degree of yellowing after UV irradiation, was characterized by focusing on compounds repressing paper recyclability using pyrolysis-gas chromatography (Py-GC) in the presence of organic alkali; tetrabutylammonium hydroxide (TBAH). Two different origin of CTMP papers prepared from different individuals of *Eucalyptus globulus* trees showing high and low yellowing after photo-irradiation was compared before UV irradiation. As a result, Many polyphenol fragments derived from both lignin and extractives were observed as 30 peaks on the pyrogram. Among these peaks, Syringol 1+6, methylsyringol 3+11, methylguaiacol 4 and vinylsyringol 7+14 were recognized as major fragments relating to photo-yellowing level in over 5 pts difference of relative molar yields between two samples. G-lignin fragment seems to enhance photo-yellowing although S-lignin fragment works vice versa. They can be used as indices for prediction of photo-yellowing level.

Keywords: Pyrolysis-gas chromatography, Mass spectrometry, Tetrabutylammonium hydroxide, *Eucalyptus globulus*, Chemithermomechanical pulp, Carbonyl group, Photo-yellowing

1. INTRODUCTION

Eucalyptus is a widely utilized species for the tree plantation, especially intended for pulp production use [1]. *E. globulus* is one of the fast growing species in a temperate zone with a period of rotation 8-10 years [2]. The breeding programs of trees are aiming to improve growth, pulp yield and strength for the pulp production because the elite tree selection contributes the reduction of pulp cost in plantations.

We have reported that several chemithermomechanical pulp (CTMP) papers prepared from individual trees of *E. globulus* showed high brightness (about 70% ISO) with over 85% pulp yield [3]. To construct an effective carbon

loop, higher paper recycling rate is preferable. The strength of CTMP papers does not decrease rapidly during recycle; however, the CTMP papers generally have a disadvantage of severe photo-yellowing occurrence by residual lignin upon photo-irradiation. The degree of photo-yellowing is crucial for recycling because it determines requirement amount of bleaching agents and is expected to be predicted by lignin structure analysis before photo-irradiation.

The characterization of lignin structure related to photo-yellowing in TMP paper before photo-irradiation was reported using high performance liquid chromatography, Fourier transform (FT) infrared

spectroscopy [4, 5] and FT-Raman spectroscopy [6] without lignin extraction. However, these spectroscopic studies have focused on the photo-yellowing mechanism and are not enough to predict the photo-yellowing level of the paper after photo-irradiation.

On the other hand, pyrolysis-gas chromatography (Py-GC) has been often used as a rapid and highly sensitive method for structural analysis of lignin [7-11]. Recently, reactive Py-GC in the presence of organic alkalis, such as tetramethylammonium hydroxide $[(\text{CH}_3)_4\text{NOH}; \text{TMAH}]$, has become a powerful method to analyze lignin and wood extractives with the polar groups, e.g., hydroxy and carboxy groups, without using any complicated pretreatments including the solvent extraction [12-14]. However, the characterization of lignin structure has not been performed effectively because the conversion of hydroxy group into carbonyl group on the ring was reported during a conventional pyrolysis [15]. Furthermore, it is difficult to determine the origin of methoxy group on the ring of the fragment using TMAH.

In this work, we have successfully characterized lignin structure causing different photo-yellowing level in CTMP papers prepared from different individuals of *Eucalyptus globulus* trees by Py-GC with tetrabutylammonium hydroxide $[(\text{C}_4\text{H}_9)_4\text{NOH}; \text{TBAH}]$, coupled to mass spectrometry (MS). Here, TBAH as a butylating reagent was used to discriminate native methoxy group on the ring from hydroxyl group.

2. EXPERIMENTAL

2.1. Samples

Two individuals of *Eucalyptus globulus* trees used in this study were grown in the same site of Western Australia (age 9.5) supplied by Department of Conservation and Land Management, Western Australia. The wood chips were pretreated with 5% sodium sulfite solution of pH 9.9 at 70°C for 1 h following at 20°C for 11 h. The primary refining was conducted at 135°C for 3 min with preheat of 5 min by a defibrator (Metso Defibrator Type D, Helsinki, Finland). The second refining was by a PFI mill (STFI, Stockholm, Sweden) using pulp consistency of 20% at clearance of 0.5 mm. The CTMP was screened by a laboratory flat screen with an 8 cut plate. Hand sheets were prepared by CTMP (called P1 and P2) and cutted off a strip of paper by scissors for the ESR measurement, furthermore, those was cryomilled into fine powders by a Spex freezer mill 6,700 (Metuchen, NJ, USA) for the Py-GC measurement.

2.2. ISO brightness

Hand sheets of CTMP were irradiated with UV light with an intensity of 0.6 mW/cm² at 365 nm for 60 min. The ISO brightness of sheets before and after UV-irradiation was measured by a spectro whiteness color meter (Suga Test Instruments SC-10W, Tokyo, Japan).

2.3. ESR measurement

Prepared papers were exposed to a low-pressure mercury lamp with an intensity of 4 μW/cm² (at wavelength range 290 nm ~ 390 nm) in the ESR quartz tube for 0 ~ 120 h. The distance between the lamp and the sample was about 50 cm. ESR spectra were observed by an X-band ESR spectrometer (JEOL JES-TE200, Tokyo, Japan), operating at 9.5 GHz with 100 kHz modulation at room temperature in air.

2.4. Py-GC and Py-GC/MS

The procedure for Py-GC is basically the same as that described previously [13]. A vertical microfurnace pyrolyzer (Frontier Lab PY2010D, Koriyama, Japan) was directly attached to a GC (Shimadzu GC17A, Kyoto, Japan) with a flame ionization detector (FID). About 200 μg of the cryo-milled samples before UV irradiation with 3 μl of TBAH aqueous solution of 40% were reactive pyrolyzed at 400°C under a flow of helium carrier gas. A metal capillary column (Frontier Lab Ultra-Alloy PY1, 30 m × 0.25 mm i.d., coated with 0.25 mm of polydimethylsiloxane through chemical cross-linking) was used. The 50 ml min⁻¹ helium carrier gas flow rate at the pyrolyzer was reduced to 1.0 ml min⁻¹ at the capillary column by a splitter (split ratio 1:25). The column temperature was programmed from 50-320°C at 5°C min⁻¹, and finally held for 20 min. The peak identification was carried out by a GC (Hewlett-Packard 6890, Avondale, PA, USA) / MS (Jeol Automass Sun 200, Tokyo, Japan) with an electron ionization source (70 eV), to which the pyrolyzer was also directly attached.

3. RESULTS AND DISCUSSION

The change of ISO brightness by UV-irradiation at 365 nm was examined for each CTMP paper prepared from two individuals of *E. globulus* trees, which both paper samples owned the almost same brightness before UV-irradiation. As in Fig. 1, the paper sample P1 showed higher brightness than P2 after UV-irradiation and P1 and P2 were used as the paper sample showing low and high yellowing level after UV-irradiation, respectively.

The change of radical intensities by UV-irradiation was also examined for P1 and P2 paper samples. Fig. 2 shows intensity changes of the observed ESR signals in the

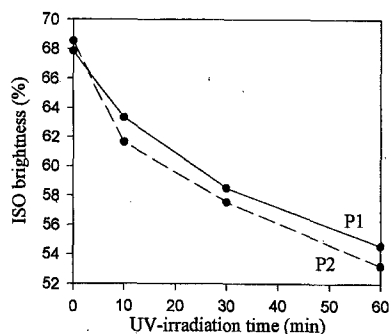


Fig. 1 Change of ISO brightness of CTMP papers by UV irradiation.

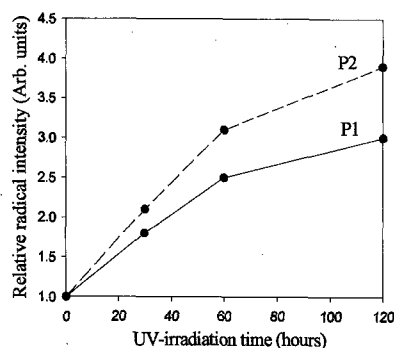


Fig. 2 Time dependency of the intensity of ESR signals produced by UV-irradiation of each CTMP papers. P1: high yellowing paper, P2: low yellowing paper.

UV-irradiated CTMP papers. As a result, the paper sample P2 showed higher radical intensities than P1 by UV-irradiation and these observed results was in fairly good agreement with that obtained by the ISO brightness. Therefore, in order to characterize of photo-yellowing trigger compounds repressing paper recyclability, P1 and P2 samples was compared before UV irradiation by

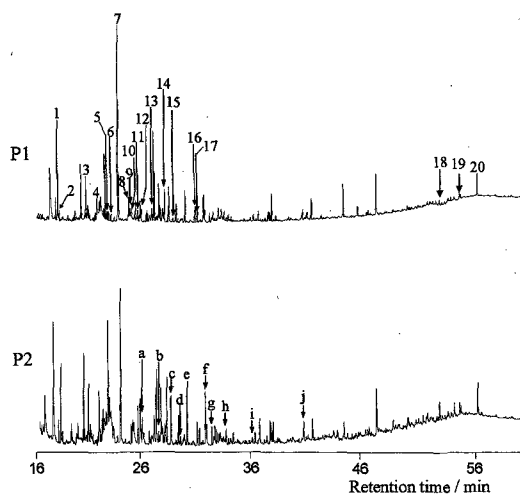


Fig. 3 Pyrograms of low (P1) and high (P2) yellowing potential CTMP paper samples, obtained at 400°C by FID in the presence of TBAH.

Py-GC with tetrabutylammonium hydroxide $[(C_4H_9)_4NOH; TBAH]$. Fig. 3 shows pyrograms of P1 and P2. Many polyphenol fragments derived from both lignin and extractives were observed as 30 peaks on the pyrogram. The peaks are classified into two groups, which are fragments without carbonyl group named as peak No. 1 - 20 and those with a carbonyl group named as peak No. a - j. Table 1 shows the assignment of these peaks by means of Py-GC / MS, together with molecular weight, estimated origin, relative molar sensitivity for FID using the effective carbon number concept [16], and relative molar yield calculated from the peak areas. Estimated origin contains syringyl- (S) and guaiacylpropane (G) units of lignin because demethoxylation would not happen during pyrolysis using [13, 17].

Table 1 Peak assignment and relative molar yield in the pyrograms of CTMP papers by Py-GC/MS.

Peak No. ^a	Compound name	MW	Estimated origin	ECN ^b	Relative molar yields ^c (%)	
					P1	P2
1	syringol	154	S-lignin	5.7	17.3	7.1
2	butoxy-3,4-dihydroxybenzene	166	tannins	8.5	0.7	0.4
3	methylsyringol	168	S-lignin	6.7	8.0	2.2
4	butoxy-methylguaiacol	194	G-lignin	10.4	3.6	21.9
5	ethylsyringol	182	S-lignin	7.7	1.3	3.9
6	butoxy-syringol	210	S-lignin	9.6	0.9	0.6
7	vinylsyringol	180	S-lignin	7.6	33.0	21.1
8	allylsyringol	194	S-lignin	8.6	2.2	2.5
9	butoxy-vinylguaiacol	206	G-lignin	11.3	0.8	1.6
10	dibutoxy-3,4-dihydroxybenzene	222	tannins	12.4	0.5	0.6
11	butoxy-methylsyringol	224	S-lignin	10.6	1.3	2.1
a	syringaldehyde	182	S-lignin	5.9	4.0	6.2
12	propenylsyringol	194	S-lignin	8.6	1.0	1.0
13	propylsyringol	196	S-lignin	8.7	2.2	1.5
b	butoxy-vanillin	208	G-lignin	9.4	0.3	0.7
14	butoxy-vinylsyringol	236	S-lignin	11.5	2.7	2.4
c	syringylacetone	210	S-lignin	7.9	6.5	7.5
15	butoxy-allylsyringol	250	S-lignin	12.5	0.3	0.3
d	butoxy-acetoguaiacone	222	G-lignin	10.6	0.4	0.5
e	butoxy-syringaldehyde	238	S-lignin	9.8	3.6	5.3
16	butoxy-propenylsyringol	252	S-lignin	12.6	1.7	1.3
17	butoxy-propenylsyringol	250	S-lignin	12.5	1.0	1.0
f	butoxy-acetosyringone	252	S-lignin	10.8	2.4	3.2
g	butoxy-syringylacetone	266	S-lignin	11.8	0.8	1.1
h	butoxy-acetoethylsyringone	266	S-lignin	11.8	0.8	1.0
i	3-methoxy-4-butoxy buthyl ester	280	G-lignin	13.2	0.2	0.1
j	3,5-dimethoxy-4-butoxy buthyl ester	310	S-lignin	13.4	0.8	1.0
18	3,3'-dimethoxy-4,4'-dibutoxystilbene	384	G-G-lignin	20.7	0.1	0.1
19	3,3',5-trimethoxy-4,4'-dibutoxystilbene	414	G-S-lignin	20.9	0.3	0.4
20	3,3',5,5'-tetramethoxy-4,4'-dibutoxystilbene	444	S-S-lignin	21.1	1.4	1.3

^aPeak number corresponds to each compound on the chromatograms in Fig. 3.

^bEffective carbon number (ECN) is for molar sensitivity corrections to FID.

^cThe molar sensitivity was calculated on the basis of ECN.

^dS = syringyl unit, G = guaiacyl unit.

As a result, syringol 1+6, methylsyringol 3+11, methylguaiacol 4 and vinylsyringol 7+14 were recognized as major fragments relating to photo-yellowing level in over 5 pts difference of relative molar yields between P1 and P2 samples. G-lignin fragment, i.e., methylguaiacol 4 was estimated at higher yield in P2 sample showing high yellowing after UV irradiation. On the other hand, all of S-lignin fragment, i.e., syringol 1+6, methylsyringol 3+11 and vinylsyringol 7+14 were estimated at higher yield in P1 sample showing low yellowing after UV irradiation. Therefore,

G-lignin fragment seems to enhance photo-yellowing although S-lignin fragment works vice versa. They can be used as indices for prediction of photo-yellowing level.

Furthermore, total 10 peaks (a - j) were assigned to a series of lignin fragments with a carbonyl group. Although almost all of them relate to photo-yellowing level positively to some extent, they are minor fragments and are not appropriate for indices to predict photo-yellowing level. Relative molar yields of stilbene structures (18 - 20) derived from lignin show almost no difference between samples.

4. CONCLUSIONS

Py with an organic alkali, TBAH was successfully applied to characterize photo-yellowing trigger compounds in CTMP papers prepared from different individuals *Eucalyptus globulus* trees. The observed results indicated that (1) syringol 1+6, methylsyringol 3+11, methylguaiacol 4 and vinylsyringol 7+14 were recognized as major fragments relating to photo-yellowing level; (2) G-lignin fragment seems to enhance photo-yellowing although S-lignin fragment works vice versa.; and (3) its yield can be used as a indices to estimate the degree of photo-yellowing for CTMP paper, in turn, to select elite trees producing the higher brightness paper with less amount of the bleaching agents even during paper recycling.

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