Characterization of Lignin Structure in Chemithermomechanical Pulp Predicting Photo-Yellowing Level by Pyrolysis-Gas Chromatography with Tetrabuthylammonium Hydroxide

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ABSTRACT

Pyrolysis-gas chromatography (Py-GC) in the presence of organic alkali of tetrabutylammonium hydroxide (TBAH) was applied to characterize the polyphenol fragments with a carbonyl group causing different magnitude of photo-yellowing in chemithermomechanical pulp (CTMP) papers. 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 photo-irradiation. As a result, 7 peaks assigned to a series of phenol compounds with a carbonyl group, derived mainly from lignin, gave significant amount of phenol compounds with a carbonyl group for the paper sample of latent high yellowing, i.e., butoxy- and syringaldehyde, butoxy- and syringylacetone, butoxy-acetoguaiacone, butoxy-acetosyringone, butoxy-acetoethylsyringone, 3-methoxy-4-butoxy butyl ester, and 3,5-dimethoxy-4-butoxy butyl ester, using Py-GC/mass spectrometry (MS). The Py-GC method combined with TBAH successfully characterized polyphenol fragments with a carbonyl group causing differ high photo-yellowing in CTMP papers using a microgram order of samples.

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 [$(CH_3)_4NOH$; 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 [$(C_4H_9)_4NOH$; TBAH], coupled to mass spectrometry (MS). Here, TBAH as a buthylating reagent was used to discriminate native methoxy group on the ring from hydroxyl group.

EXPERIMENTAL

Samples

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 and cryomilled into fine powders by a Spex freezer mill 6,700 (Metuchen, NJ, USA) prior to Py-GC measurement.

ISO brightness

Hand sheets of CTMP were irradiated with UV light at 265 nm for 60 min. The ISO brightness of sheets before and after photo-irradiation was measured by a spectro-whiteness color meter (Suga Test Instruments SC-10W, Tokyo, Japan).

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 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 μm 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.

RESULTS AND DISCUSSION

The change of ISO brightness by photo-irradiation at 265 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 photo-irradiation. As in Table 1, the paper sample P1 showed higher brightness than P2 after photo-irradiation and P1 and P2 were used as the paper sample showing low and high yellowing level after photo-irradiation, respectively.

Table 1 Change of ISO brightness of CTMP papers by photo-irradiation

Sample	ISO Brightness (%) Duration of exposure (min)			
	0	10	30	60
P1	67.85	63.34	58.52	54.57
P2	68.54	61.64	57.57	53.20

Fig. 1 shows chromatograms of P1 and P2. Many polyphenol fragments derived from both lignin and extractives were observed as 30 peaks on the chromatogram. 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**.

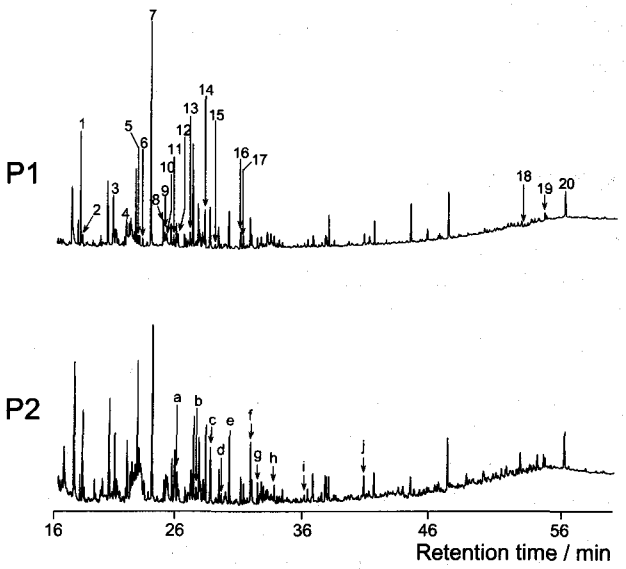

Fig. 1 Chromatograms of low (P1) and high (P2) yellowing potential CTMP paper samples, obtained at 400°C by FID in the presence of TBAH.

Table 2 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 2 Peak assignment and relative molar yield in the chromatograms of CTMP papers by Py-GC/MS

Peak No.[a]	Fragment	Relative molar yield (%)[b]	
		P1	P2
1	syringol	17.3	7.1
2	butoxy-3,4-dihydroxybenzene	0.7	0.4
3	methylsyringol	8.0	2.2
4	butoxy-methylguaiacol	3.6	21.9
5	ethylsyringol	1.3	3.9
6	butoxy-syringol	0.9	0.6
7	vinylsyringol	33.0	21.1
8	allylsyringol	2.2	2.5
9	butoxy-vinylguaiacol	0.8	1.6
10	dibutoxy-3,4-dihydroxybenzene	0.5	0.6
11	butoxy-methylsyringol	1.3	2.1
12	propenylsyringol	1.0	1.0
13	propylsyringol	2.2	1.5
14	butoxy-vinylsyringol	2.7	2.4
15	butoxy-allylsyringol	0.3	0.3
16	butoxy-propylsyringol	1.7	1.3
17	butoxy-propenylsyringol	1.0	1.0
18	3,3'-dimethoxy-4,4'-dibutoxystilbene	0.1	0.1
19	3,3',5-trimethoxy-4,4'-dibutoxystilbene	0.3	0.4
20	3,3',5,5'-tetramethoxy-4,4'-dibutoxystilbene	1.4	1.3
a	syringaldehyde	4.0	6.2
b	butoxy-vanillin	0.3	0.7
c	syringylacetone	6.5	7.5
d	butoxy-acetoguaiacone	0.4	0.5
e	butoxy-syringaldehyde	3.6	5.3
f	butoxy-acetosyringone	2.4	3.2
g	butoxy-syringylacetone	0.8	1.1
h	butoxy-acetoethylsyringone	0.8	1.0
i	3-methoxy-4-butoxy buthyl ester	0.2	0.1
j	3,5-dimethoxy-4-butoxy buthyl ester	0.8	1.0

[a]Peak number corresponds to each fragment on the chromatograms in Fig. 1.
[b]The molar sensitivity was calculated on the basis of effective carbon number for molar sensitivity corrections to FID.

As a result, syringol **1**, methylsyringol **3**, methylguaiacol **4** and vinylsyringol **7** were recognized as major fragments relating to photo-yellowing level in over 5 pts difference of relative molar yields between two samples. The 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.

On the other hand, 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.

CONCLUSIONS

Py with an organic alkali, TBAH was successfully applied to characterize polyphenol fragments with a carbonyl group causing different photo-yellowing in CTMP papers prepared from different individuals *Eucalyptus globulus* trees. The observed results indicated that (1) 7 peaks were assigned to a series of phenol compounds with a carbonyl group derived mainly from lignin; (2) the high yellowing paper gave significant amount of phenol compounds with a carbonyl group than the low yellowing paper; (3) the observed polyphenol fragments with a carbonyl group derived from S-lignin were very different between CTMP papers because of inter-individual differences of original woods, (4) its yield can be used as a index 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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