ANALYSIS OF LIGNIN BY PYROLYSIS-GAS CHROMATOGRAPHY I EFFECT OF INORGANIC SUBSTANCES ON GUAIACOL-DEWATIVE YIELD FROM SOFTWOODS AND TWIR LIGNINS

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ABSTRACT

  To obtain lignin-derived pyrolysis products in larger yields. Curie-point pyrolysis was performed on the softwood species Japanese red pine (Pinus densiflora Sieb. et Zucc.), Japanese cedar (cryptomeria japonica D. DON) and Japanese cypress (Chamaecyparis obtusa Endl.), and their dioxane lignins treated with various inorganic substances, over the temperature range 358-764   . The resulting guaiacol derivatives (guaiacol, 4-methyl-, 4-ethyl- and 4-vinylguaiacols, eugenol, vanillin, cis- and trans-isoeugenol, and acetovanillone) were determined by gas chromatography.

  The softwood samples sandwiched between two sheets of heat-resistant filter paper made of borosilicate glass fibers yielded from 1.56 to 1.64 times more guaiacol derivatives than unsandwiched samples. Sandwiching the dioxane lignins between heat-resistant papers also increased the guaiacol-derivative yield. by 13 to 27%.

  The sandwich-2 method developed in this study is widely applicable as a sample preparation method for increasing the yield of lignin-derived products on Curie-point pyrolysis. Gas chromalo8rqhy; glass fiber. borosilicate; guaiacol derivatives; lignin;   pyrolysis, Curie-point., softwoods.

INTRODUCTION

  Pyrolysis combined with gas chromatography (Py-GC) is a powerful tool

for synthetic and natural polymer analysis. Early applications of Py-GC in

lignin analysis can be found in the reports of Kratzl et al. [1] and Kitao and

Watanabe [2], who suggested that this method offered a convenient analyti-

cal technique for the rapid characterization of a very small amount of lignin.

Despite obvious advantages, the Py-GC method has been largely neglected compared with other lignin degradation techniques such as acidolysis, alkaline nitrobenzene oxidation and permanganate oxidation, which are time-consuming and demand large sample amount.

The development of modern analytical instruments has recently resulted in the publication of a number of reports describing the possibility and the usefulness of the Py-GC method for lignin characterization [3-8]. In these reports, investigators separated and identified many guaiacyl and syringyl derivatives, and predicted that the Py-GC method would be extensively used in various areas of lignin chemistry in the future. Boon et al. [6l pointed out that combined Curie-point pyrolysis-GC/ MS (mass spectrometly) is an interesting microanalytical characterization method for plant material and its derived fractions. However, few reports [7,8] are available oft: the quantitative determination of the resulting volatile phenols. In particular, we have found no reported attempts to increase the yield of lignin-derived phenols.

The object of the present study was to increase the guaiacol-derivative yield by pyrolyzing softwoods a lignins in the presence of inorganic substances. To our knowledge, there are few reports [9] dealing with the exact relationship between inorganic substances and the yield of lignin-derived pyrolysis phenols, whereas considerable documentation exists on the effects of inorganic salts on cellulose from the viewpoint of the development of fire-retardant chemicals [10-16].

A sample. preparation method for increasing the yield of lignin-derived pyrolysis phenols was also developed. This method is applicable to the Curie-point pyrolysis of all lignocllulosic materials.

. EXPERIMENTAL

Materials

The extractive-free softwoods used in this study were Japanese red pine (Pinus densiflora Sieb: et Zhcc.), Japanese cedar (Crypyomeria japonica D. Don) and Japanese cypress (Chamaecyparis obtusa Endl.). Dioxane lignins (DLs) from these softwoods were prepared by the method of Pepper et al. [17].

The commercial inorganic salts used were potassium carb6hate, sodium tetraborate, sodium carbonate, boron trioxide, sodium chloride, nickel, aluminium oxide, silicic anhydride and calcium oxide.

Three types of heat-resistant filter paper made of glass fibers (GB100R)/ and silica fibers (QR100 and 80) were supplied by the Advantec TOYO Co.

Pyrolysis

Pyrolysis unit and gas chromatography

A Curie-point pyrolyzer (JHP-2 model, Japan Analytical Industry Co.) was coupled directly with a gas chromatograph (GC) (Shimadzu GC-14A). Each sample, prepared as described below, was wrapped with a ferromagnetic pyrofoil and kept in the pyrolyzer at 140 for 5 min (wood) or 1 min (DL samples), after the unit had been flushed with helium for 15 s. The samples were then pyrolyzed by induction heat for 4 s, and the resulting volatile compounds were transferred to the GC. The GC analysis was run on a 25 m Thikote fused-silica capillary column (0.53 mm I.D.) with a chemically bonded methyl silicone coating 5.0 μ m thick (Quadrex Corp.). Helium was used as carrier gas. The temperature program used was 1 min at 70 , and 4 /min from 70 to 250 , after which isothermal conditions were maintained. The injection port and the flame ionization detector (FID) were kept at 260 . The peak areas were measured by an integrator (Shimadzu Chromatopac C-R6A). Identification of peaks was carried out by comparison with retention times of known substances and/or using a Py-GC/MS system (Finnigan MAT ITD-800) fitted with a 30 m fused-silica capillary column (0.25 mm I.D.) with a 0.25 μ m film chemically bonded Durabond DB-5 coating (J. & W. Scientific Inc.). Known amounts of authentic guaiacol-derivative solutions were injected into the pyrolyzer and transferred into GC without pyrolysis to obtain exact retention times and calibration curves for the quantitative determination of guaiacol derivatives.

Sample preparation for pyrolysis

(a) Standard method. About 0.5 mg of the starting material was weighed precisely, wrapped with a pyrofoil, and subjected to Py-GC.

(b) Addition method. The salt or the glass fiber paper powder (about 50 mg) was added to the starting material (0.5 mg) on a pyrofoil. The prepared sample was subjected to Py-GC.

(c) Mixing method. The salt or the glass fiber paper powder was mixed with the starting material by grinding in a vibratory sample mill (Model TI-1, Hirako Seisakusyo) for 5 min. The mixture, containing 0.5 mg of the starting material, was wrapped with a pyrofoil, and then pyrolyzed.   .

(d) Sandwich-1 method. The starting material (0.5 mg) on a glass fiber paper was wrapped with a pyrofoil, and then pyrolyzed.

(e) Sandwich-2 method. The starting material (0.5 mg) was sandwiched between two Pieces of glass fiber paper, wrapped with a pyrofoil, and then pyrolyzed.
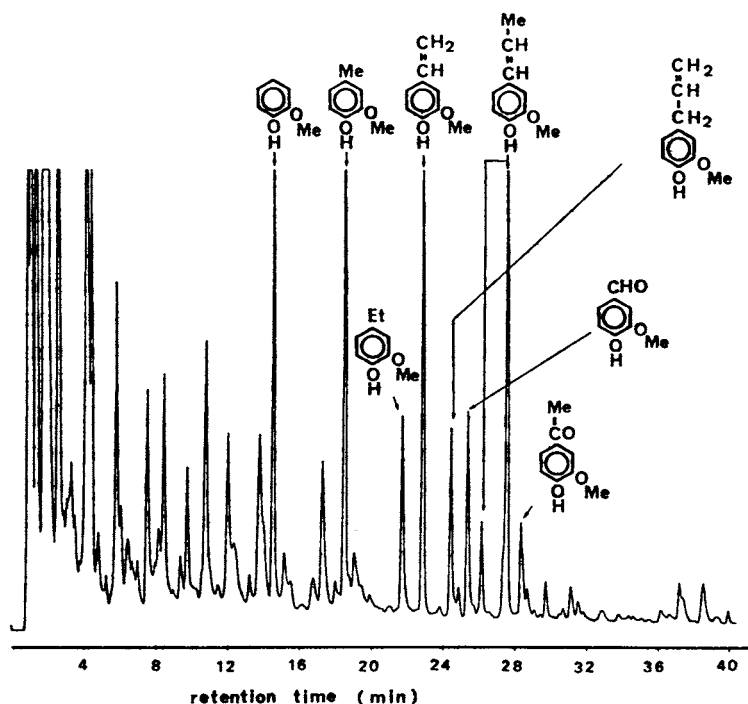
Fig. 1 Pyrogram of Japanese red pine wood at 500°C for 4 s (conditions are given in the text)

RESULTS AND DISCUSSION

A typical pyrogram of the volatile compounds from pine wood at 500
is shown in Fig. 1. The pyrograms of pine wood treated with and without
inorganic substances were qualitatively identical. The main pyrolysis prod-
ucts were the nine guaiacol derivatives guaiacol, 4-methyl-, 4-ethyl- and
4-vinylguaiacol, eugenol, vanillin, cis-and trams-isoeugenol, and acetovanil-
lone, which confirms previous work as reported by Kitao and Watanabe [2],
who pyrolyzed pine milled wood lignin under similar conditions. In addition
to these guaiacol derivatives, small amounts of 4-propylguaiacol, vanillic
acid and propiovanillone were also identified. Contrary , to the reports of
Obst [5], Boon et al. [6] and Faix et al. [7,8], coniferaldehyde and coniferyl
alcohol were rarely detected under the conditions used in the present work.
Peaks of phenols, xylenols and cresols   often overlapped those of
carbohydrate-derived compounds.

Effects of inorganic substances on pyrolysis

Table 1 shows the effects on the pyrolysis of pine woods at 500   of
various inorganic substances, selected according to the classification of Tang

TABLE 1

Effects of inorganic substances on pyrolysis of Japanese red pine wood at 500°C for 4 s.

Inorganic substance	Yield of guaiacol derivatives (%) [a]	
	A [b]	B [c]
GB100R [d]	13.66	12.00
Na_2CO_3	12.85	12.21
K_2CO_3	12.82	4.73
None [e]	11.79	11.79
$Na_2B_4O_7$	11.34	trace
Al_2O_3	11.09	trace
SiO_2	10.01	11.77
CaO	9.43	3.25
NaCl	8.26	9.78
B_2O_3	1.52	4.51
Ni	—	10.39

[a] Weight % based on Klason lignin.
[b] Mixing method (inorganic substance : pine wood = 0.25 : 1).
[c] Addition method.
[d] Glass fiber paper (pulverized).
[e] Standard method.

[11]. The yield from pine wood in the absence of inorganic substances (standard method) is also shown, as a control. The guaiacol-derivative yield is expressed as a sum of the yields of guaiacol, 4-methylguaiaco1, 4-ethyl-plus 4-vinylguaiaco1, eugenols (eugenol and *cis-* and *trans-*isoeugenol) and carbonyl compounds (vani1lin, and acetovanillone).

From the data in Table 1, the borosilicate glass fiber paper (GB100R), sodium and potassium carbonates were effective in increasing the total yield of guaiacol derivatives. Mixing with the glass fiber paper increased the guaiacol-derivative yield by about 1.9% compared with that of pine wood alone (standard method). Sodium and potassium carbonates also increased the guaiacol-derivative yield by about 1.0%, despite the finding of Gardner et al. [9] that sodium carbonate did not increase the yield of pyrolysis products. This discrepancy is probably due to their having determined only four pyrolysis products, and also to the different pyrolysis conditions employed. The addition of pulverized GB100R and sodium carbonate to pine wood produced no serious increase in the 8uaiacol-derivative yield compared with that from the standard method, but the addition of potassium carbonate greatly decreased the guaiacol-derivative yield (4.73%).

Upon mixing with the carbonates in the sample rhil1. the samples took on a strong yellowish colour. This suggests that the pine wood reacted with the carbonates during grinding, and the resulting sample partly decomposed before pyrolysis. Sodium chloride slightly decreased the guaiacol-derivative yield. In this connection, Richards et al. [16] detected polyhydroxybenzenes
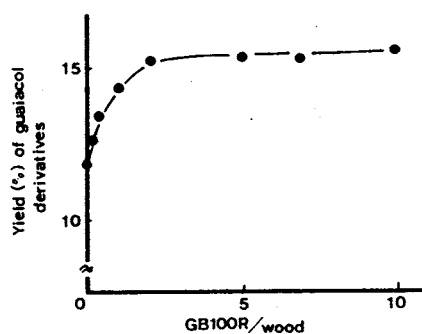
Fig. 2. Effects of the glass fiber paper (GB100R) to wood ratio on pyrolysis of Japanese red pine wood at 500 °C for 4 s by the mixing method. Note: Yield is weight % based on Klason lignin.

from the pyrolysis of cellulose in the presence of sodium chloride, probably because they pyrolyzed at lower temperature for a longer time add trimethylsilylated pyrolysis products prior to GC analysis.

Therefore, we concluded that of the procedures tested in the present study, the glass fiber paper (GB100R) method was the most effective for catalyzing pyrolysis.

Figure 2 shows the change in the guaiacol-derivative yield on pyrolysis (at 500) of pine wood mixed with pulverized GB100R. The yield clearly increased on mixing with small amounts of GB100R powder, and gradually increased further with increasing amounts of GB100R. However, the yield appeared to level off after reaching about 15.20% at ratio of GB100R to pine wood 2.0. Consequently, the largest yield of guaiacol derivatives obtained by the mixing method was 15.76% at the ratio of 10.0. Thus, Fig. 2 shows that it is technically difficult to obtain the guaiacol derivatives with a yield larger than 16.0% from pine wood by the mixing method.

Effects of sample preparation method on pyrolysis

Figure 3 shows guaiacol-derivative yields from pine samples prepared by various methods. Pine wood sandwiched between two pieces of GB100R (i.e. the sandwich-2 method) gave the largest yield (18.86%), whereas the sandwich-1 method gave 15.32%, a value similar to that obtained by the mixing method.

From these findings, the effects of the sample preparation methods on the guaiaco1-derivative yield are ordered as follows: sandwich-2 method > mixing method = sandwich-1 method > addition method = standard method. The largest yield of guaiacol derivatives obtained by the sandwich-2 method was due to the increase of guaiaco1, 4-vinylguaiacol and eugenols, although we cannot explain the mechanism of this effect at this stage.
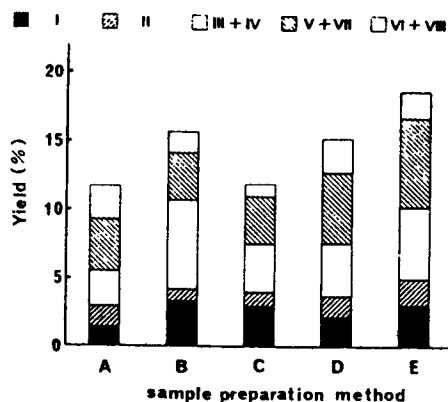
Fig. 3. Effects of sample preparation method using GB100R on pyrolysis of Japanese red pine wood at 500°C for 4 s. (I) guaiacol, (II) 4-methylguaiacol, (III) 4-ethylguaiacol, (IV) 4-vinylguaiacol, (V) eugenol, (VI) vanillin, (VII) isoeugenol, (VIII) acetovanillone; (A) standard method, (B) mixing method (GB100R:wood =10:1), (C) addition method, (D) sandwich-1 method, (E) sandwich-2 method. Note: Yield is weight % based on Klason lignin.

Effects of heat-resistant filter paper on pyrolysis

The effects of types of heat-resistant filter paper on pyrolysis (at 500) of pine woods prepared by the sandwich-2 method are shown in Fig. 4. Although pine wood sandwiched with QR100 also gave guaiacol derivatives in moderately good yield (15.44%), this was smaller than the yield obtained with GB100R. The yield with QR80, which contains alumina as binders, was only 3.40%. Therefore, the effects of the heat-resistant filter papers on the guaiacol-derivative yield when pyrolysis was performed by the sandwich-2
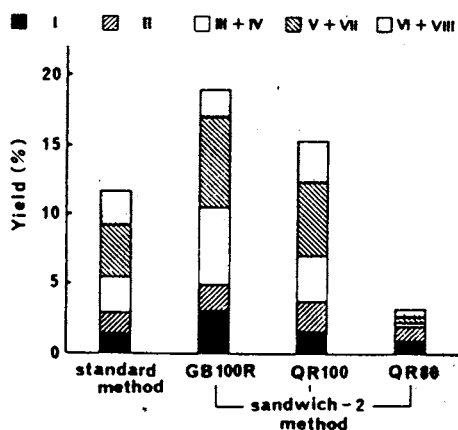

Fig. 4. Effects of heat-resistant filter paper on pyrolysis of Japanese red pine wood at 500°C for 4 s. GB100R, glass fiber paper; QR 100 and 80, silica fiber paper. Note: Yield is weight % based on Klason lignin. Compound numbers and names refer to those in Fig. 3.

method are ordered as follows: GB100R > QR100 > untreated (11.79%) > QR80. One reason for this great difference in the yield lies in the principal constituents of the various papers. GB100R is made of borosilicate glass, whereas QR100 and 80 are mainly made of silic acid. Thus, the above result agrees well with the data in Table 1.

Effect of temperature on pyrolysis

The effects of temperatures in the rang 358-764   on the pyrolysis of pine wood, alone and sandwiched with GB100R, were also investigated (Fig. 5).

The most useful finding was that the guaiacol-derivative yield was largest at 500   , regardless of whether or not the pine samples were sandwiched with GB100R. Thus, 500   is the optimum pyrolysis temperature. Below 590   the guaiacol-derivative yields obtained from pine woods sandwiched with GB100R were much larger than those from the untreated woods. At 670 and 764   ,I adverse results were obtained. Particularly at 764oC, the sandwiched sample gave a much smaller yield of the guaiacol derivatives, and a more complicated pyrogram, with many peaks, than that obtained by the standard method. This indicates that GB100R may catalyze pyrolysis of guaiacol derivatives into smaller fragments at this temperature.

Extensive degradation at a higher temperature has been reported by Nozawa and Satonaka [18]. These authors pyrolyz8d Japanese oak (*Quercus mongolica var. grosseserrata*) at 400 and 800   and observed large mounts of phenol and cresol, while guaiacol derivatives were not among the pyroly-sis products obtained at 800   . Therefore, the small yield of guaiacol derivatives from our pyrolysis at 764   is probably due to extensive conversion of the initially produced guaiacol derivatives into other degrada-
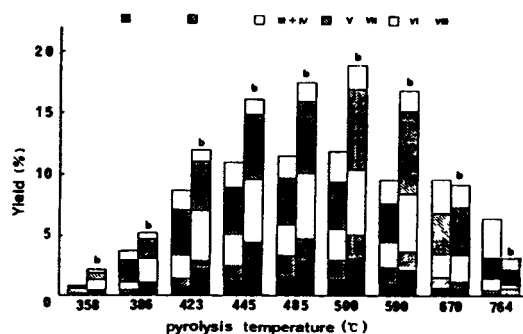

Fig 5 Effects of temperature on pyrolysis of Japanese red pine wood for 4 s (a) standard method (b) sandwich 2 method using GB100R Note Yield is weight % based on Klason lignin Compound numbers and names refer to those in Fig 3

tion products such as catechol and cresol. Influence of pyrolysis temperature on the composition of the product mixture will be discussed elsewhere.

From the above results, the most suitable conditions for our purpose were (a) to sandwich the sample with GB100R, and (b) to pyrolyze the sandwich at 500 .

Application of sandwich-2 method to other samples

The sandwich-2 method using GB100R was ,applied to the pyrolysis of other softwoods and their DLs at 500 .

The total yield of guaiacol derivatives increased from 13.97 to 22.85% for Japanese cedar, and from 13.50 to 21.03% for Japanese cypress, as compared with the standard method (Fig. 6). Thus, the guaiacol-derivative yields from Japanese cedar and cypress sandwiched with GB100R were increased by 1.64 and 1.56 times, respectively, over those from the untreated woods. These values agree very closely with those (1.60 times) obtained for the pyrolysis of Japanese red pine.

A similar tendency was observed for the pyrolysis of DL samples sandwiched with GB100R (Fig. 7). The guaiacol-derivative yields from DLs sandwiched with GB100R were 5.53% for pine, 7.68% for Japanese cedar and 7.01% for Japanese cypress, whereas those from untreated DLs were 4.37, 6.55 and 6.17%, respectively. Thus, the sandwich-2 method using GB100R increased the guaiacol-derivative yields from DLs 1.27 times for pine, 1.17 times for Japanese cedar and 1.13 times for Japanese cypress, over those from the untreated DL samples. However, the amounts oft guaiacol derivatives obtained from the DLs were reduced to one-third of those from
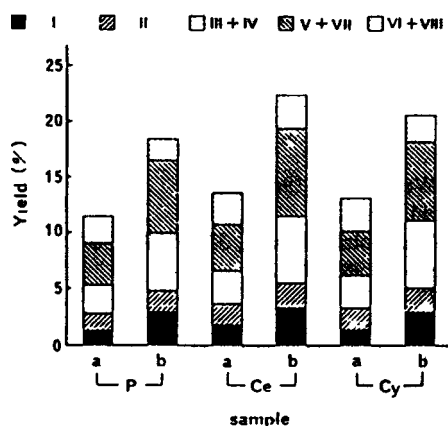

Fig 6 Pyrolysis of some softwood species at 500°C for 4 s (P) Japanese red pine (Ce) Japanese cedar (Cy) Japanese cypress (a) standard method (b) sandwich 2 method using GB100R Note Yield is weight % based on Klason lignin Compound numbers and names refer to those in Fig 3
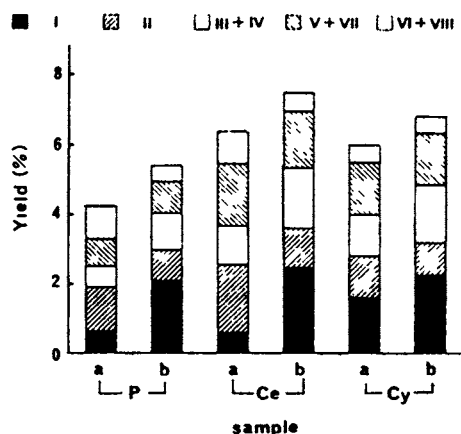
Fig 7 Pyrolysis of softwood dioxane lignins (DLs) at 500°C for 4 s (P) Japanese red pine DL, (Ce) Japanese cedar DL, (Cy) Japanese cypress DL, (a) standard method, (b) sandwich-2 method using GB100R Note Yield is weight % based on the starting material Compound numbers and names refer to those in Fig 3

the corresponding softwoods, probably as a result of modification of the chemical structure of lignin during the isolati6n process.

The above results suggest that the sandwich-2 method using GB100R could be widely applied to the Curie-point pyrolysis of many softwood species and their lignin preparations.

ACKNOW LEDGEMENTS

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