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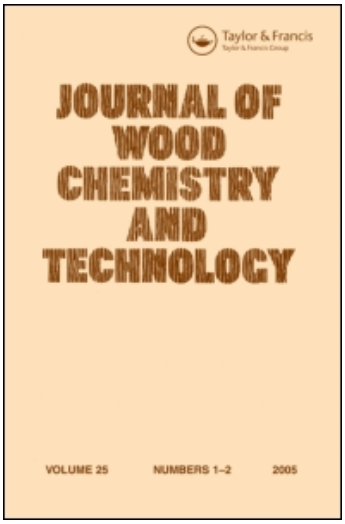

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F. A. Agblevor[a]; D. G. B. Boocock[a]
[a] Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada

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THE ORIGINS OF PHENOL PRODUCED IN THE RAPID HYDROTHERMOLYSIS AND ALKALINE HYDROLYSIS OF HYBRID POPLAR LIGNINS

F. A. Agblevor and D. G. B. Boocock
Department of Chemical Engineering and Applied Chemistry
University of Toronto
Toronto, Ontario, Canada M5S 1A4

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ABSTRACT

Hybrid poplar lignins were isolated from selected hybrid poplar clones by an enzymatic/solvent extraction method. The lignins were subjected to both rapid hydrothermolysis (RHT) and alkaline hydrolysis. Phenol (C_6H_5OH) was the predominant component of hydrothermolysis products, whilst p-hydroxybenzoic acid (PHBA) was the chief product of the alkaline hydrolysis. Phenol yields were 2-9 wt.% of the lignin , whilst PHBA yields ranged from 3-6 wt.% of the lignin. The yields of both products were sensitive to the poplar clone. When PHBA was similarly subjected to the RHT process, it decarboxylated to phenol quantitatively. Thus the phenol observed in the RHT products derives mostly from the PHBA esters in the lignin. The PHBA is linked to the lignin by ester and/or ether bonds. PHBA linkages are cleaved hydrolytically and the resultant acid then decarboxylates to phenol.

INTRODUCTION

The conversion of renewable lignocellulosic materials into liquid fuels and chemicals has been of great interest, particularly after the oil crisis of the 1970's. Over the past decade, thermochemical and biochemical technologies have been developed to exploit this potential source of fuels and chemicals. One area

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which has been a subject of several research papers is the thermal conversion of lignin and other biomass materials into phenolics. However, most investigators have found that, although lignin yields a variety of phenols, no particular component is significantly predominant[1]. Researchers such as Panasyuk[2] discovered that, among the phenols from softwood lignin, guaiacol is dominant, whereas cresols are predominant in annual plants. Actual phenol was obtained in only small quantities. Even in the improved Noguchi process, the best yields were 3% phenol, 4% o-cresol, 6% m/p-cresols in a total monophenol yield of 21%. There were at least 10 to 15 phenolic compounds in the product[3].

Studies in our laboratory[4,5,6] have revealed that when hybrid poplar wood chips are liquefied under rapid hydrothermolysis conditions, a significantly higher yield of phenol is obtained. Yields as high as 4-6% by mass of dry wood were observed in some cases. The upper figure is surprising given that it corresponds to a yield of 24% based on the lignin. Unfortunately, the poplar clone which gave the 6% yield was not available for the study reported in this paper. The amount of phenol produced appeared to be sensitive to both the poplar clone and the pH. It was also revealed[6] that the holocellulose fraction of the wood did not contribute to the phenol production under the rapid hydrothermolysis (RHT) conditions. The phenol was produced from only the lignin fraction of these woods. Our studies[6] also revealed that, under RHT conditions, guaiacyl and syringyl groups do not demethoxylate. Furthermore, it is known[7] that phenol does

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not occur as a separate entity in poplar wood. This raised the question of whether poplar wood lignins are structurally different from other hardwood lignins. Thus the purpose of this study is to ascertain the origin of the phenol and the mechanism of its formation during the liquefaction process. Besides being of theoretical interest, the mechanism of phenol formation is of practical interest to the pulp and paper industry, since poplar species are now being pulped in some semi-chemical sulfur-free processes. The presence of appreciable quantities of phenol in the pulping effluent is undesirable from the environmental point of view.

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EXPERIMENTAL

Materials

The Ontario Ministry of Natural Resources Laboratory (Maple, Ontario, Canada) supplied the following poplar species for this project:

C147 (P.x canescens), GA93 (P.grandidentata x alba), AG186 (P.alba x grandidentata), DN30 (P x euramericana), DN38 (P.deltoides v."Virginiana" x 'Volga Poplar' NE-238.), N743 (P.nigra), AK42 (P.alba x glandulosa), DTAC1 (P.angulata x berolinensis), and I45/51 (P. x euramericana).

All these species were ten to twelve years old except for DN30 which was five years old.

Enzymatic/Solvent Extraction of Lignin

The substrates were debarked, air-dried and separated into sapwood and heartwood. The sapwood was Wiley-milled to -40 mesh

and extracted with 5% EDTA solution. The iron free milled wood was Soxhlet extracted with toluene/ethanol mixture (2:1 v/v) for 48 hours. Further extraction was carried out with 95% ethanol for another 48 hours. The samples were washed with hot water and air-dried. Further drying was done over P_2O_5. The extractive-free dry milled wood was ball-milled in a ceramic ball mill for 72 hours in toluene. The milled product was filtered, and the solid was extracted with dioxane/water mixture (9:1 v/v) for 48 hours. The extract was evaporated under reduced pressure to dryness. The resultant crude lignin was purified by the Bjorkman[8] procedure and freeze-dried from aqueous dioxane. The residue was washed thoroughly with water and hydrolysed with Celluclast 1.5 L enzyme (Novo Enzyme, Montreal, Quebec). The hydrolysis conditions were: 50°C, acetate buffer pH 4.6, and 72 hours incubation time with continuous shaking (150 rpm) in an orbital shaker bath. After 72 hours, the hydrolysate was centrifuged, then fresh buffer and enzyme were added and hydrolysis continued for another 72 hours. Thereafter, the hydrolysate was centrifuged, the solid residue washed with water and extracted with aqueous dioxane as described above. The crude lignin was purified by dissolving it in 90% acetic acid and precipitating into distilled water. The fluffy precipitate was centrifuged and freeze-dried from water. Elemental analysis, methoxyl content and spectral data (IR, proton and C-13 nmr) confirm that this material is 90-95% pure lignin.

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Alkaline Hydrolysis

About 100 mg of lignin and 2 M NaOH(10 mL) were charged into a 15 mL stainless steel tubular reactor which was then flushed with

nitrogen, and sealed. The reactor was immersed in a fluidised sand bath and rocked gently at a constant temperature of 150 ± 2°C for two hours and then quenched in water and allowed to cool to room temperature. The reaction products were acidified with dilute hydrochloric acid (1:1, v/v) to pH 3.0, filtered, and extracted with diethyl ether (5 x 50 mL). The extract was dried with $MgSO_4$, evaporated under reduced pressure to dryness and quantified. The product was redissolved in diethyl ether and methylated with diazomethane. The methylated compounds were analysed on an HP 5880A gas chromatograph under the following conditions:

Column: J & W Fused silica, DB-17, 30 m x 0.516 mm, 1.0 µm film thickness.

Detector: FID, 240°C

Carrier gas: Helium, 8 mL/min.

Injection temperature: 230°C.

Oven temperature: 120°C for 5 min. and 5°/min to 240°C.

Internal Standard: Isovanillin.

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Rapid Hydrothermolysis

Lignin:

Lignin (250 mg) and water (1.25 mL) were loaded into a 10 mL stainless steel tubular reactor equipped with swagelock fittings. The reactor was flushed with nitrogen, sealed and immersed in fluidised sand bath. The reaction temperature was monitored by a K-thermocouple inserted in the reactor. The contents of the reactor were heated rapidly to 350°C within 2-3 min. As soon as

reactants attained the desired temperature (350°C), the reactor was quickly quenched in water and allowed to cool to room temperature.

The reaction products were separated into aqueous and oil phases. The aqueous phase was extracted with diethyl ether (3 x 50 mL), dried with $MgSO_4$ and gas chromatographed under similar conditions as described above. The oil phase was dissolved in acetone, filtered, evaporated under reduced pressure and quantified. The acetone-soluble oil was fractionated by the scheme shown in Figure 1. The fractions were analysed by gas chromatography on a fused-silica column under similar conditions used for the alkaline hydrolysis products, except anisole was used as internal standard.

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p-Hydroxybenzoic Acid

About 100 mg of pure p-hydroxybenzoic acid (PHBA) (BDH Chemicals Ltd., Toronto, Ontario) and water (0.5 mL) were charged into a 10 mL stainless steel tubular reactor and hydrothermolysed as described above. The reaction products were extracted with diethyl ether (3 x 50 mL), dried with $MgSO_4$ and analysed by gas chromatography on a fused silica column under similar conditions as the alkaline hydrolysis products. Anisole was used as internal standard. The products were also analysed by GC/MS.

RESULTS AND DISCUSSION

Since it has been shown that the guaiacyl and syringyl units in lignin do not demethoxylate during rapid hydrothermolysis[9], it was hypothesized that the phenol precursor in lignin (hereafter

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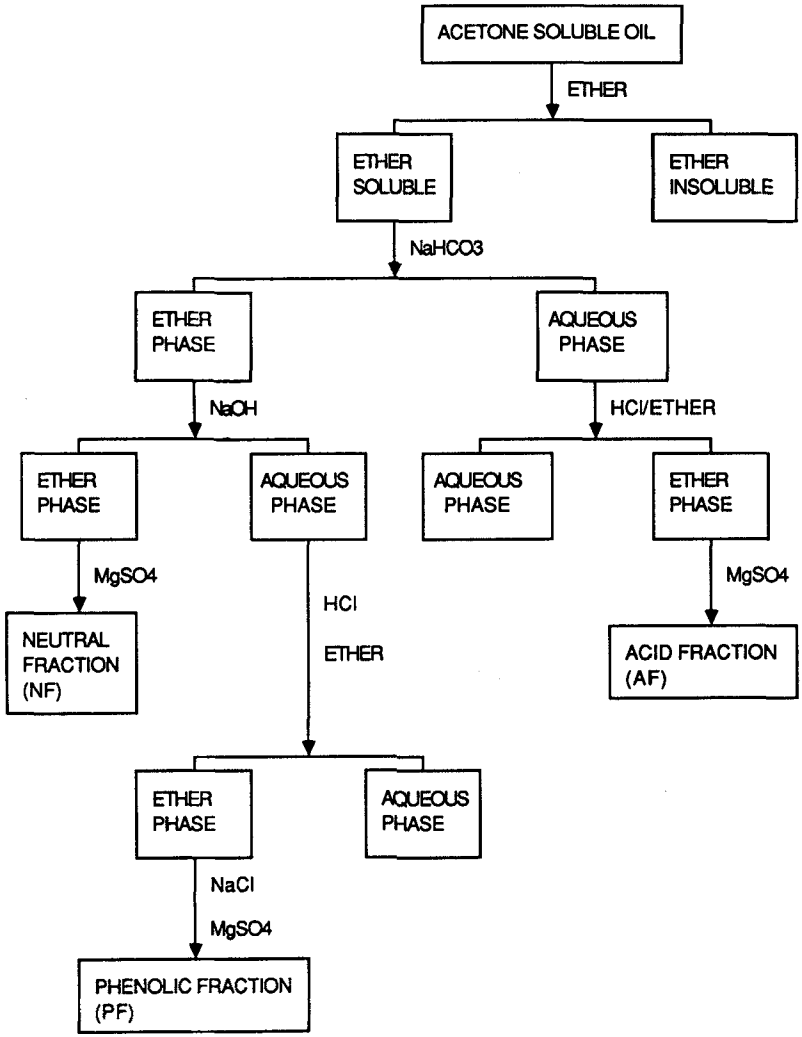

FIGURE 1: Scheme for Fractionating RHT Products

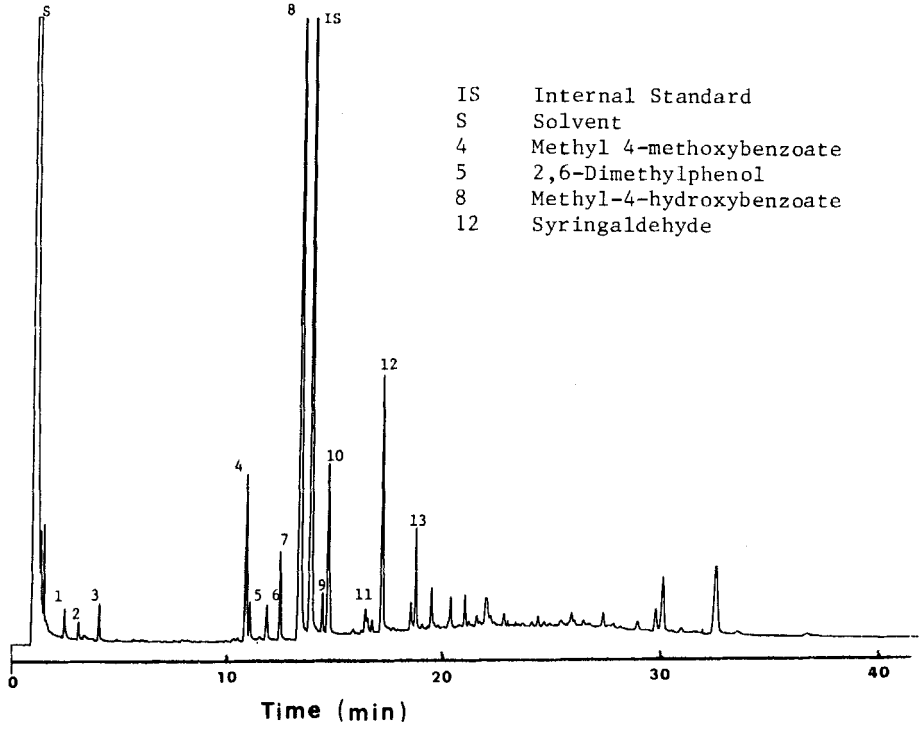

FIGURE 2: Gas Chromatograph of Methylated Alkaline Hydrolysis Products (150°C)

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referred to as the phenolic moiety) existed as part of a p-hydroxyphenyl propane unit and/or p-hydroxybenzoic acid unit ester-linked to the phenylpropane side chain. A combination of alkaline hydrolysis, nitrobenzene oxidation and RHT was used to test the hypothesis and thus clarify the origin of the phenol.

The alkaline hydrolysates of the selected hybrid poplar clones were qualitatively similar. Typical gas chromatograms of the methylated products are shown in Figures 2 and 3. Peaks

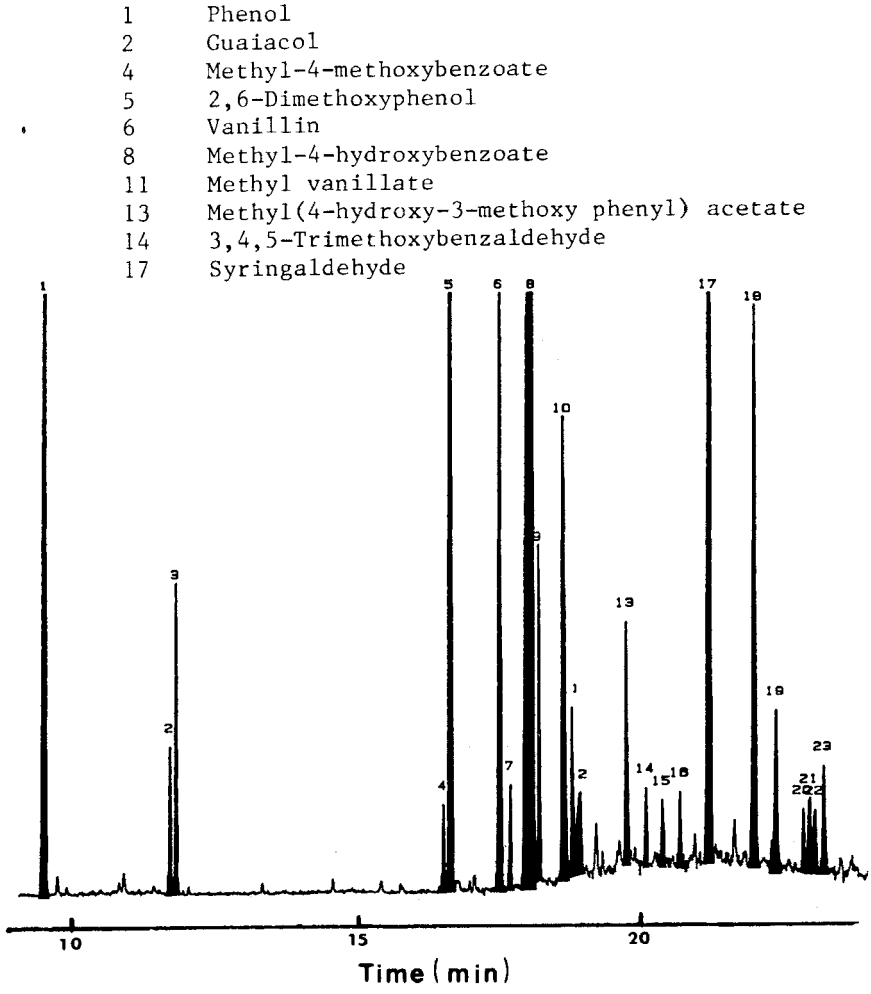

FIGURE 3: GC/MS of Methylated Alkaline Hydrolysis Products (180°C)

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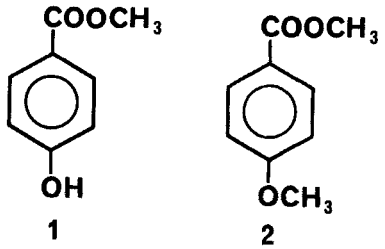
characteristic of PHBA, benzoic, vanillic, and syringic acids as well as syringyaldehyde, vanillin, and 2,6-dimethoxyphenol were identified by comparison of their mass spectra and GC retention times data with those of authentic samples in the computer library. Several other minor unidentified peaks were also present. Depending upon the degree of methylation, PHBA produces two



methylated structures (1 and 2 below). Both compounds were identified in the methylated products (peaks 8 and 4, respectively, in Figure 3). Thus, for quantification of PHBA, the peak area from both structures 1 and 2 must be used. For samples methylated several times, compound 1 disappeared from the gas chromatogram.

The GC trace of the alkaline hydrolysates clearly show PHBA (peaks 4 and 8, Figures 2 and 3) as the predominant compound in the mixture. Although, the hydrolyses at 150°C and 180°C produced a similar slate of compounds, the latter had an additional peak (peak 1 in Figure 3) which was identified as phenol. The yields of PHBA from the selected hybrid poplar clones are summarized in Table 1.

The detection of PHBA in the hydrolysate agrees with the works of Smith[10], Pearl[11], Okabe[12], Nakano[13], Nakamura[14], and Sarkanen[15]

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TABLE 1

Alkaline Hydrolysis Products of Lignins (150°C)

Sample Clone	Unreacted Material (%)	ESM* (%)	PHBA (%)
GA93	46.9	37.1	4.5
AK42	50.3	19.3	3.6
AG186	50.1	19.0	4.7
DN30	52.5	21.1	4.2
DTAC1	41.3	23.1	5.1
C147	46.4	19.6	5.7
I45/51	50.2	24.1	4.8
DN38	45.3	32.0	6.2
N743	40.9	19.3	6.2

*ESM = Ether Soluble Material
Unreacted material = Residue after hydrolysis

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which also showed that the phenolic moiety existed in poplar lignin as a PHBA carboxyl ester O-bonded to the alpha and gamma carbons of the phenylpropane unit. Although the published literature has indicated the existence of PHBA as an ester in lignin, there is very little data on significant phenol production due to PHBA in pulping liquors, pyrolysis reactions or hydrothermolysis reactions. What is interesting about the detection of this compound in the alkaline hydrolysate is the correlation between the PHBA produced in the alkaline hydrolysis and the phenol produced in the RHT. This correlation can be seen by comparing the gas chromatograms of the phenolic (PF) and the aqueous phase ether soluble (APES) fractions (Figures 4 and 5) from the RHT products with the methylated hydrolysate chromatograms (Figure 2). In the former,

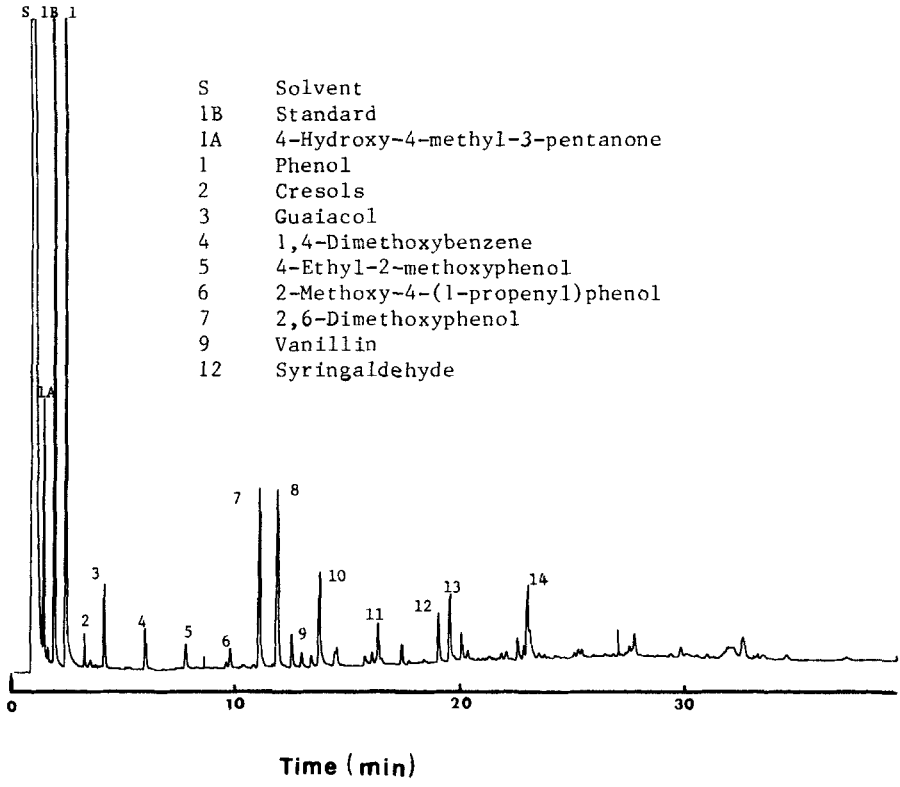

FIGURE 4: Gas Chromatograph of Phenolic Fraction of RHT Products

phenol (peak 1) is the dominant component in both fractions, whereas in the latter PHBA is predominant. The correlation has an r value of 0.87 (Figure 9). The total yield of phenol from fractions PF and APES (Table 2) is quite significant, whereas only traces of PHBA were detected in the methylated acidic fractions of the RHT products (Figure 6). The absence of PHBA in the methylated acidic fractions suggests that either this acid underwent secondary

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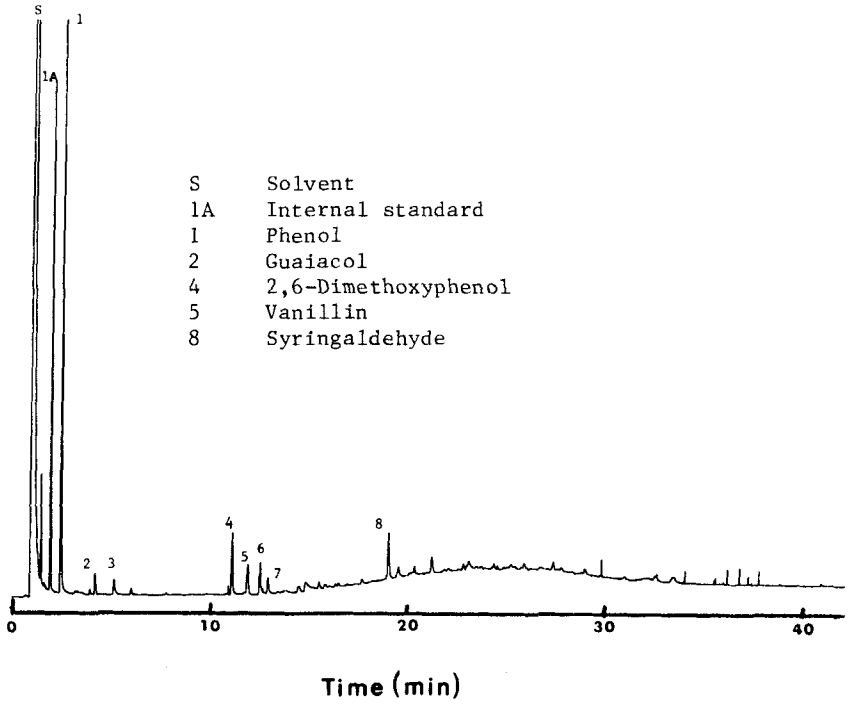

S Solvent
1A Internal standard
1 Phenol
2 Guaiacol
4 2,6-Dimethoxyphenol
5 Vanillin
8 Syringaldehyde

FIGURE 5: Gas Chromatograph of APES

TABLE 2

Rapid Hydrothermolysis (RHT) Products of Lignins

Sample Clone	ASO (%)**	ESO (%)	APES (%)	PF (%)	AF (%)	NF (%)	Phenol* (%)
GA93	76.7	30.9	4.7	17.0	2.8	4.7	4.2
AK42	77.7	32.1	6.5	8.0	2.5	5.0	2.7
AG186	80.8	32.1	5.5	9.7	4.4	4.7	3.2
C147	83.4	32.1	19.2	8.5	5.2	5.7	7.1
DTAC1	67.9	33.0	5.1	18.6	6.7	4.8	5.6
DN30	67.5	36.9	4.3	19.8	5.2	6.0	2.3
I45/51	67.7	19.3	5.7	5.3	3.6	3.8	3.6
DN38	77.4	33.7	5.1	12.5	5.3	4.5	9.5
N743	76.1						9.0
PHBA	----	----	68.1	----	---	---	67.0

*Phenol in PF + Phenol in APES
** Expressed as wt.% of Lignin
ASO = Acetone-Soluble Oil
ESO = Ether-Soluble Oil
PF = Phenolic Fraction
AF = Acidic Fraction
NF = Neutral Fraction

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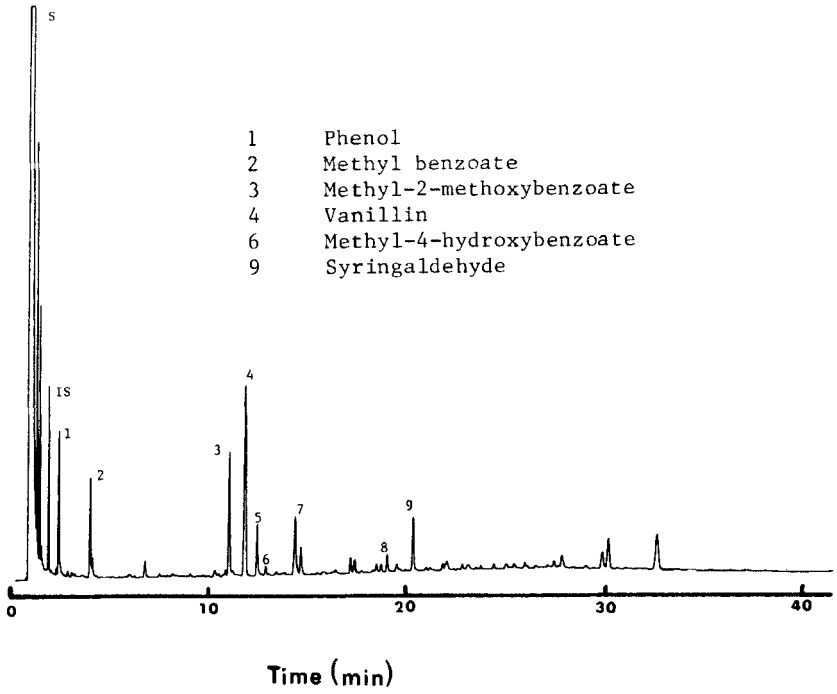

FIGURE 6: Gas Chromatograph of Acidic Fraction of RHT Products

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reactions after its formation in the RHT process or it was not produced at all. The latter hypothesis is unlikely, since PHBA was detected in significant quantities in the acidic fractions of RHT reactions at lower temperatures (300°C) by the authors[9]. Examination of the gas chromatograms of the ether extract of PHBA RHT products (Figure 7) reveals the nature of this secondary reaction. Phenol (identified by GC/MS) is the only phenolic product, and it is formed quantitatively from the PHBA (Table 2). This evidence implies that any PHBA formed on hydrothermolysing poplar lignin

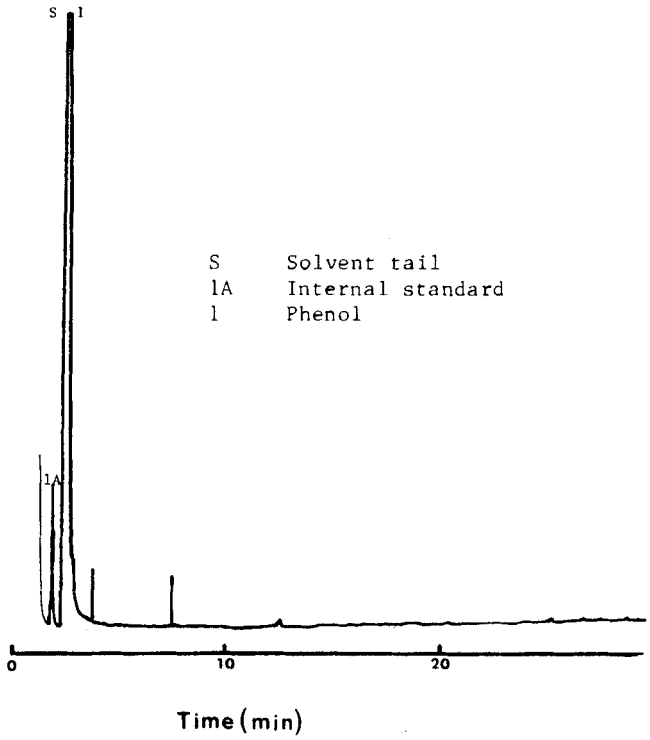

FIGURE 7: Gas Chromatograph of PHBA RHT Product

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will be converted into phenol, and the yield of phenol will depend on the rate of PHBA formation from its esters. The observation of phenol in the alkaline hydrolysate at a higher temperature (180°C) and its absence at the lower temperature (150°C) also lends support to this argument. However, as pointed out by Whiting[16], phenol can also be produced from the p-hydroxy-phenylpropane moieties in the lignin. Data from the nitrobenzene oxidation of our lignins did not show that these moieties were contributors to the phenol

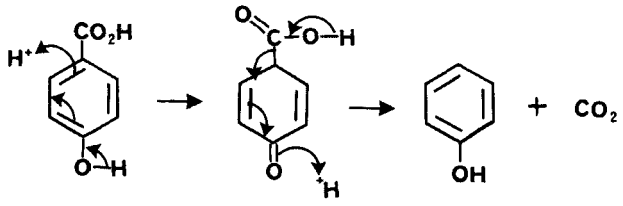

FIGURE 8: Decarboxylation of PHBA to Phenol

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production[17]. In fact, the phenol yield from the RHT run was 4 to 6 times the p-hydroxybenzaldehyde (the alkaline nitrobenzene oxidation product of the p-hydroxyphenyl propane moiety) content of the lignin. Thus the phenol in the lignin RHT products derives mostly from the thermal decarboxylation of PHBA which was, in turn, produced from the PHBA esters. Further evidence for the origin of the phenol is provided by Azim[18] who has shown independently that significant quantities of phenol detected in poplar pulping effluents derived from PHBA. The acid catalysed ionic decarboxylation mechanism is shown in Figure 8. The decarboxylation of PHBA and other aromatic hydroxycarboxylic acids depends on pH, with pH 7.8 being the optimum value[19]. However, below pH 3.8, the reaction was independent of pH. The same workers discovered that the maximum hydrolysis rate of methyl, ethyl, and n-propyl 4-hydroxybenzoate esters occur at the mid-pH range. These reaction conditions are similar to the initial neutral conditions that prevail in RHT processes, thus favouring the maximum production of PHBA. The dependence of both the hydrolysis and the

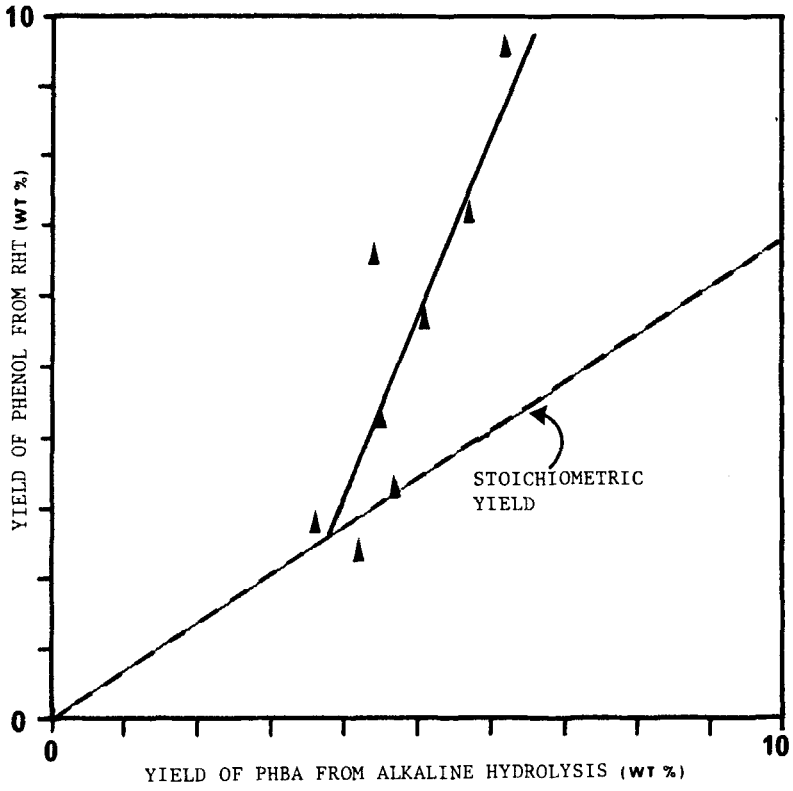

FIGURE 9: Yield of Phenol from RHT versus Yield of PHBA from Alkaline Hydrolysis for Hybrid Poplar Lignins

decarboxylation reactions on pH explains the sensitivity of the phenol yields to pH as observed in our earlier publications[6].

It is interesting to note that, although there is a linear correlation between PHBA produced by alkaline hydrolysis of lignins and the phenol produced by the RHT of lignins (Figure 9), it is not the expected stoichiometric (1:1) relationship. There is, for some of the clones, more phenol produced by the RHT process than the

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equivalent PHBA obtained by alkaline hydrolysis of the lignin. Thus there are some phenol producing moieties which are resistant to alkaline hydrolysis but labile to hydrothermolysis. Since these moieties are only significant when the PHBA yield rises above 4%, it is tempting to propose that other bonds (e.g., ether) between the PHBA and lignin unit become statistically more likely. The work of Smith[10], dismissed the existence of any other linkages other than ester bonds between PHBA and lignins. However, Okabe and Kratzl[12], in their experiments with cell-free systems, found some evidence indicating that PHBA, in dehydrogenation polymers, forms ester and ether linkages and probably some carbon-carbon bonds. This evidence was contradicted by Venverloo's work[20]. The above RHT results tend to lend support to Okabe's suggestion. To test for PHBA linkages which are resistant to alkaline hydrolysis, some lignin samples were saponified with 2 M NaOH at room temperature in a nitrogen atmosphere for 24 hours, and another sample was saponified at 150°C for 2 hours. After acidification and centrifugation, the recovered lignins were dried and hydrothermolysed. The phenolic fraction of the RHT products exhibited a strong phenol peak on the gas chromatogram. This evidence shows the presence of linkages to the PHBA which are resistant to alkaline hydrolysis, but are labile on hydrothermolysis, to yield phenol. This supports the data shown in Figure 9.

During the investigation of the effect of alkaline medium on the selective hydrolysis of p-hydroxy benzyl aryl ether bonds in model compounds, Adler[21] observed that p-hydroxy- and p-methoxy-

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benzyl ethers of saccharides were not split by 1 M NaOH at 25°C/24 hours. At conditions (170°C/2 hours, 2M NaOH) more severe than those used in our hydrolysis experiment, Grier et al[22] showed that benzyl aryl ether bonds will only cleave if a quinone methide can be formed. This requires that there be a phenolic OH group para to the benzyl group. Other researchers[23] have made similar observations. Thus, it follows that any PHBA linked to the lignin macromolecule by ether bonds would resist alkaline hydrolysis even at 150°C/2 hours, whereas ester bonds will split very readily. On the other hand, Hemmingson[24] has shown that at least 50% of beta-O-4 linkages in lignin are broken by steam treatment of hardwood at 210°C/1.7 MPa. Since alpha-aryl ether bonds are weaker than beta-O-4 bonds, it is reasonable to assume that any alpha-aryl ether linkages present in the lignin will also be cleaved. A similar mechanism can, therefore, be applied to the interpretation of the rapid hydrothermolytic degradation (at 350°C) of the residual alkaline hydrolysis product. It can be supposed that PHBA-alpha-ether linkages are cleaved by the action of steam on the lignin during the RHT process. The resultant PHBA then decarboxylates to phenol.

Since no other phenol producing moieties (apart from PHBA) have been identified in poplar lignins, the RHT evidence implies that a significant amount of PHBA in high yielding phenol hybrid poplar clones are linked to lignin by ether bonds and perhaps carbon-carbon bonds as suggested by Okabe and Kratzl[12]. Further work on the exact nature of this bond is underway in our laboratory.

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The results in Tables 1 and 2 also clearly point to a correlation between the amount of phenol and PHBA formed and the type of hybrid poplar clone. The DN38 clone gave the highest yield of phenol (9.5%) which also produced a high amount of PHBA (6.2%). On the other hand, the AK42 clone produced significantly lower amounts of both phenol (2.7%) and PHBA (3.6%). Interestingly, the hybrids which are cross-breeds of P.nigra and some other poplar species have higher PHBA and phenol yields than other hybrids. It appears that the P.nigra species influences the biosynthesis of PHBA esters in the hybrid wood. The pure P.nigra (N743) species itself has a relatively high PHBA content (6.2%). These results also confirm our previous findings[6] on the sensitivity of the phenol yield to the poplar clones. It is still not understood how cross-breeding influences the PHBA ester formation in these woods.

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CONCLUSION

The experiments have shown that the amount of phenol produced when hybrid poplar lignins are hydrothermolysed is directly related to the p-hydroxybenzoate ester content of the lignin. Hybrid poplar clones, such as AK42, which contain lower amounts of this compound produce lower quantities of phenol. Hybrid clones which are cross-breeds between P.nigra and some other poplar species tend to have higher PHBA content than other hybrids. For high phenol yielding hybrid poplar clones, some of the PHBA appears to be ether linked to the lignin macromolecule. In view of the present research efforts toward maximizing phenolics production from wood

and other lignocellulosic materials, the information contained here will help in selecting appropriate wood species for both wood liquefaction and other thermochemical conversion processes. Furthermore, since poplar, including some hybrid poplar, is currently being pulped for the manufacture of corrugating medium by a sulfur-free semi-chemical process[18], this information may have an important bearing on the choice of clone which will minimize the phenol content of the pulping effluents.

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