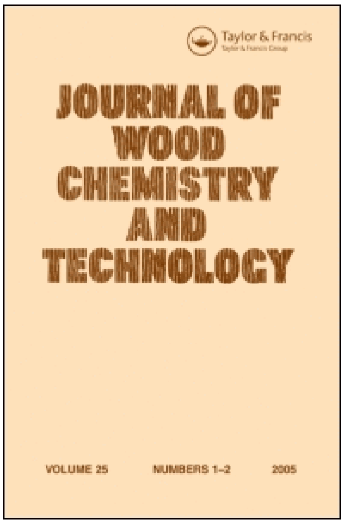


**Journal of Wood Chemistry and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# Rapid Hydrothermolysis of Poplar Wood: Comparison of Sapwood, Heartwood, Bark, and Isolated Lignin

R. Krishna Mohan Rao Kallury[a]; Thomas T. Tidwell[a]; Foster A. Agblevor[b]; David C. B. Boocock[b]; Martin Holysh[b]
[a] Department of Chemistry, University of Toronto, Ontario, Canada [b] Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada

**To cite this Article** Kallury, R. Krishna Mohan Rao , Tidwell, Thomas T. , Agblevor, Foster A. , Boocock, David C. B. and Holysh, Martin(1987) 'Rapid Hydrothermolysis of Poplar Wood: Comparison of Sapwood, Heartwood, Bark, and Isolated Lignin', Journal of Wood Chemistry and Technology, 7: 3, 353 — 371

**To link to this Article: DOI:** 10.1080/02773818708085274

**URL:** http://dx.doi.org/10.1080/02773818708085274

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 7(3), 353-371 (1987)

# RAPID HYDROTHERMOLYSIS OF POPLAR WOOD: COMPARISON OF SAPWOOD, HEARTWOOD, BARK, AND ISOLATED LIGNIN

R. Krishna Mohan Rao Kallury and Thomas T. Tidwell
Department of Chemistry
University of Toronto
Toronto, Ontario, Canada M5S 1A1

and

Foster A. Agblevor, David G. B. Boocock and Martin Holysh
Department of Chemical Engineering and Applied Chemistry
University of Toronto
Toronto, Ontario, Canada M5S 1A5

## ABSTRACT

Rapid hydrothermolysis at 350°C of poplar sapwood, heartwood and bark, as well as the lignin extracted from the sapwood and heartwood, gives oil and water soluble fractions whose chemical analysis is correlated with the nature of the feed stock. Results from cellulose and Douglas fir are included, and the poplar bark and heartwood lignin are shown to give an ether soluble oil that consists mainly of guaiacyl units while the sapwood product is mainly syringyl. However, the chloroform soluble oil from both sapwood and heartwood was mainly syringyl with the additional presence of carbohydrate derived material in the heartwood oil. The acetone-only soluble residue from sapwood was shown by pyrolysis mass spectrometry to be mainly cellulose derived while that from heartwood was mainly from lignin. Thus there is a fundamental difference in the behaviour of the poplar sapwood and heartwood that may arise from different distributions of the guaiacyl and syringyl units, and of the binding to the cellulose. The origin of the rapid hydrothermolysis products with respect to the major wood components is discussed. An empirical approach to the calculation of the lignin content based on the rapid hydrothermolysis fractions is presented.

## INTRODUCTION

The thermochemical and biochemical conversion of wood and its constituents to materials useful as fuels and chemical raw materials have been the object of extensive investigations in recent years[1-4]. The connection between the composition of the products of these processes and the chemical structure of the constituents of the wood, principally lignin, cellulose and hemicellulose, and the morphological regions of the wood (heartwood, sapwood and bark) are of fundamental importance for understanding the details of wood conversion and have been an area of active interest[5-12].

The current study applies the rapid hydrothermolysis technique to this problem. This recently developed[13-15] method avoids the use of catalysts or reagent gases at high pressures as well as long residence times at high temperatures and so minimizes secondary reactions of the initial wood degradation products. This technique has already been applied to an isolated lignin from poplar wood[16], cellulose and related carbohydrates[17], and hemicellulose[18], and the nature of the resultant products determined, but no systematic understanding of the relationship between the chemical composition of the product and that of the different constituents and morphological regions of the reactant have emerged. The goal of the present investigation is to provide this understanding.

## RESULTS

The hydrothermolysis of poplar sapwood, heartwood and bark as well as isolated lignins from both the sapwood and the heartwood were carried out using the rapid heat-up system previously described[15]. For comparison whole wood from Douglas fir was also examined.

The reaction products consisted of aqueous and oil phases which were separated, and the former extracted with ether to give the aqueous phase ether-solubles while the oil phase was dissolved in acetone, filtered, and evaporated. This oil phase was successively extracted with ether and then chloroform to give the ether-soluble oil, the chloroform-soluble oil, and the acetone-only-soluble oil. The ether extract of the oil phase was extracted first with sodium bicarbonate and then with sodium hydroxide and evaporated to give three fractions, and the yields of all these fractions are reported in Table 1. Previous results for cellulose[19] are also included.

The different fractions were analysed using the procedure reported previously[20], including $^1$H- and $^{13}$C-NMR, FTIR, GC and GC/MS. The acetone-only soluble residue was also subjected to pyrolysis mass spectrometry. The results of these studies are summarized in Tables 2-4, and are discussed individually below for the different fractions obtained.

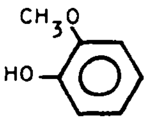
## DISCUSSION

### Ether-Soluble Oil Phase

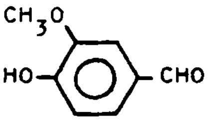
The sodium hydroxide extract of the ether-soluble oil from poplar bark, heartwood and sapwood equalled 7.8, 3.5 and 7.3%, respectively, of the original feedstock (Table 1) and consisted of phenols (Table 2) which can be classified as of either guaiacyl (e.g., 1 - 3) or syringyl (e.g., 4 - 6) type with relative guaiacyl:syringyl product ratios of 2.8:1, 1.6:1, and 1:2.4, respectively.

In comparison, Douglas fir, a softwood whose lignin is almost exclusively guaiacyl type[7], gave 4.4% of a phenolic fraction with a 16:1 ratio of guaiacyl:syringyl components (Table 2). Thus the poplar bark and heartwood resemble Douglas fir in giving mainly guaiacyl type phenols, whereas poplar sapwood is distinctively different in giving a large phenolic fraction that is predominantly syringyl in character.

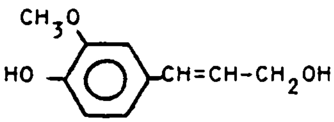
The composition of the phenolic fractions from the isolated lignins were similar to those of the corresponding parent sapwood



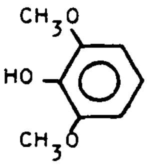
1 (guaiacol)



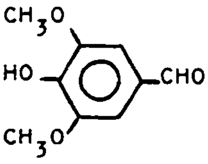
2 (vanillin)



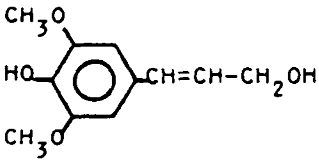
3 (coniferyl alcohol)



4 (syringol)



5 (syringaldehyde)



6 (synapyl alcohol)

and heartwood, respectively, shown in Table 2. Futhermore, the yields of the sodium hydroxide-soluble phenolic fractions from the isolated lignins were 3.3 and 4.0 times as great as when the corresponding sapwood and heartwood were used, which is consistent with the fact that the composition of the wood is approximately 24% lignin, 52% cellulose, 21% hemicellulose, and 3% extractives[21,22]. These results indicate that essentially all of the phenolic products are lignin-derived, and this is consistent with the fact that very little phenolic material is formed from the hydrothermolysis of cellulose[19]. The phenolic fraction from sapwood is also twice as large as that from heartwood whether the whole wood is used or if the lignins are first separated out.

Our results are in general agreement with those of Bobleter and Concin[23], who effected hydrothermolysis of isolated poplar and spruce lignin above 300°C and recovered about 10% of the original material as monomeric aromatics, and identified 20 individual compounds by mass spectrometry and comparison of VPC retention

TABLE 1

Fractions from Rapid Hydrothermolysis of Poplar Constituents at 350°C*

| Feedstock | Acetone-Soluble | Ether-Soluble Oil |  |  |  | Chloroform Soluble Oil | Residue† | Aqueous phase Ether Soluble |
|---|---|---|---|---|---|---|---|---|
|  |  | Total | $NaHCO_3$ Soluble | NaOH Soluble | Neutral |  |  |  |
| Poplar Sapwood | 43 | 13 | 3.0 | 7.3 | 3.9 | 17 | 12 | 10 |
| Poplar Heartwood | 48 | 7 | 1.5 | 3.5 | 2.0 | 18 | 22 | 12 |
| Poplar Bark | 37 | 13 | 3.0 | 7.8 | 2.2 | 4 | 20 | 8 |
| Poplar Sapwood lignin | 88 | 28 | 2.8 | 23.8 | 1.4 | 57 | 3 | 3 |
| Poplar Heartwood lignin | 67 | 14 | 1.4 | 11.2 | 1.4 | 40 | 12 | 4 |
| Cellulose | 30 | trace |  |  |  | 11 | 19 | 15 |
| Douglas Fir | 41 | 9 | 2.2 | 5.0 | 1.8 | 4 | 28 | 9 |

* w/w %

† material soluble in acetone but not in ether or chloroform

## TABLE 2

Composition of the Phenolic Fractions
from the Ether-Soluble Oils*

| Phenol | Sapwood | Heartwood | Bark | Douglas Fir |
|---|---|---|---|---|
| Phenol | 5 | 7 | 6 | 5 |
| Cresols | 1 | 1 | 2 | 3 |
| Ethylphenols | 2 | 1 | 2 | 3 |
| Propylphenols | 5 | 4 | 6 | 2 |
| Allylphenols | 1 | 1 | 4 | 2 |
| Vinylphenols | 1 | 1 | 3 | 1 |
| Guaiacol | 5 | 11 | 8 | 20 |
| Methylguaiacols | 1 | 2 | 3 | 4 |
| Ethylguaiacols | 1 | 4 | 6 | 5 |
| Propylguaiacols | 2 | 4 | 8 | 7 |
| Allylguaiacols | 4 | 3 | 2 | 3 |
| Vinylguaiacols | 2 | 2 | 2 | 2 |
| Vanillin | 5 | 13 | 15 | 22 |
| Vanillic acid | 1 | 1 | 2 | 3 |
| Coniferyl alcohol | 2 | 6 | 6 | 4 |
| Homovanillin | 1 | 2 | 2 | 4 |
| Homovanillic acid | 1 | 1 | 1 | 2 |
| Syringol | 10 | 8 | 4 | 1 |
| Methylsyringols | 2 | 2 | 1 | 1 |
| Ethylsyringols | 2 | 2 | 4 | 1 |
| Propylsyringols | 3 | 2 | 4 | 1 |
| Allylsyringols | 4 | 1 | 2 | tr† |
| Vinylsyringosl | 3 | 1 | tr | tr |
| Syringic aldehyde | 18 | 4 | 3 | 1 |
| Sinapyl alcohol | 8 | 1 | 1 | tr |
| Syringyl alcohol | 5 | 2 | 1 | tr |
| Syringic acid | 2 | tr | tr | tr |
| Homosyringic aldehyde | 2 | 1 | tr | tr |

* figures in wt.% of the phenolic fraction
† tr = trace

TABLE 3

Composition of the $NaHCO_3$-Solubles
from the Ether-Soluble Oils*

| Substance | Sapwood | Heartwood | Bark | Douglas Fir |
|---|---|---|---|---|
| Benzoic acid | 10 | 16 | 51 | 5 |
| Vanillic acid | 2 | 11 | 13 | 38 |
| Homovanillic acid | 1 | 4 | 3 | 12 |
| Syringic acid | 31 | 5 | 1 | tr |
| p-Hydroxybenzoic acid | 5 | 4 | 2 | 6 |
| Dihydroxybenzoic acid | 3 | 4 | 2 | 1 |
| Phenol | 1 | 1 | 1 | 1 |
| Cresols | tr | 1 | 1 | 1 |
| Ethylphenols | tr | 1 | 1 | tr |
| Guaiacol | tr | 3 | 2 | 3 |
| Catechol | 1 | 3 | 4 | 4 |
| Methylcatechols | 2 | 1 | 2 | 4 |
| Unidentified | 20 | 25 | 10 | 10 |

* wt.% of the $NaHCO_3$-solubles from the ether-solubles

times. The structural identifications were similar to those of Table 2, and the spruce lignin led mainly to guaiacyl-type products.

Bobleter and Concin[23] also detected most of the phenolic acids we have identified in the sodium bicarbonate extract from the ether-soluble oil (Table 3). However, they did not report aliphatic acids from lignin and those we detect from the wood-based oils (Table 3) are evidently derived from the cellulose.

There is evidence that the neutral fractions from the ether-soluble oils are derived from the extractives present in the original wood. Thus, these extractives are reported to be complex mixtures of mono-, di- and tri-glycerides of fatty acids, together with fatty acids and alcohols and other esters[24]. These fractions displayed 90% of their $^1$H-NMR integration in the $\delta$ 0.8 to 2.5 region corresponding to aliphatic protons, their FTIR spectra showed strong carbonyl absorption at 1720-1740 cm$^{-1}$ and alcoholic hydroxyl peaks at 3200-3400 cm$^{-1}$, and their EIMS showed patterns characteristic of straight aliphatic chains[25].

## Chloroform-Soluble Oil Phases

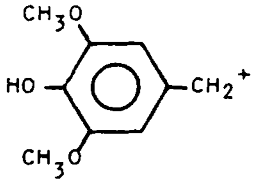
Poplar sapwood and heartwood both give 17-18% of chloroform-soluble material based on the initial substrate (Table 1), but as discussed below these differ in spectroscopic properties. Poplar bark and Douglas fir in contrast give less than a fourth as much of this material. As shown in Table 1, the rapid hydrothermolysis of the isolated lignins and cellulose both give rise to significant amounts of this fraction, and, if the whole wood behaves similarly to the isolated components, both the lignin and cellulose will contribute to the chloroform extracts. As discussed below, this assumption gives a satisfactory quantitative account of the product yield.

The FTIR of the chloroform-soluble oil fraction from poplar wood or lignin showed strong absorptions at 1230 and 1330 cm$^{-1}$, bands assigned to the syringyl moiety[12], but only weak absorption for the guaiacyl bands[12] at 1040 and 1270 cm$^{-1}$. In contrast the corresponding fraction from Douglas fir exhibits strong guaiacyl absorption in its FTIR spectrum.

The $^1$H-NMR spectra of the chloroform-soluble oils from poplar lignins show characteristic absorption in the aromatic ($\delta$ 6.2-7.2), phenolic OH ($\delta$ 5.4-5.8) and methoxyl ($\delta$ 3.6-4.0) regions but very little between $\delta$ 1.0-3.0, whereas the chloroform fractions from poplar sapwood, heartwood and Douglas fir show 10, 40 and 50% of their total $^1$H integrations in this latter region. This $\delta$ 1.0-3.0 absorption is evidently due to carbohydrate-derived material, and in our study of cellulose hydrothermolysis[19] a series of products were identified which give rise to absorption in this region, including levulinic acid and its lactones, 5-methyl furfural and methyl cyclopentenones.

The $^{13}C$-NMR spectra of the chloroform-soluble oils from poplar sapwood and heartwood and from the isolated lignins are all similar and show characteristic $C_{Ar}$(and $C_{olefinic}$) and $C_{MeO}$ absorption at δ 100-140 and 54-54 ppm, respectively, in integrated ratios of 4.5:1 for sapwood, 7:1 for heartwood and 4:1 for the isolated lignins, with weak absorption at δ 60-63 ppm and very little between δ 63-90 ppm. Use of the integrated areas of the δ 103-108 region assigned[26] to the unsubstituted C-2,6 of syringyl aryl rings and the δ 110-115 region characteristic[26] of C-2 of the guaiacyl ring gave a 4:1 syringyl:guaiacyl ratio for all these oils.

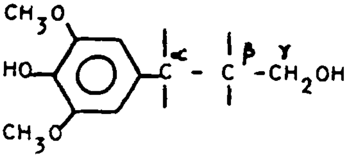
The mass spectrum of the chloroform-soluble oils all showed a strong peak at m/z 167, assignable to the $C_9H_{11}O_3$ fragment (a) expected to be a major fragment from many syringyl structures.



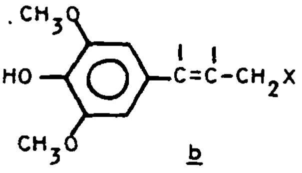
a

Thus the chloroform-soluble oil phase from poplar sapwood or heartwood or the isolated lignins are indicated by FTIR to contain predominantly syringyl derived products from the lignins, while the $^{1}H$-NMR indicates that the poplar heartwood oil differs significantly from that from sapwood but resembles that from Douglas fir in also having major absorption in the region δ 1.0-3.0. The $^{13}C$-NMR evidence for the 103-115 region corroborates the FTIR evidence in showing a strong predominance of syringyl over guaiacyl units present, and the oils from the isolated lignins both give 4:1 ratios of $C_{Ar}$ to $C_{MeO}$, close to the 3:1 ratio expected for a purely syringyl type product and indicating a predominance of this unit. The heartwood derived oil differs from the sapwood material in having a higher $C_{Ar}:C_{MeO}$ ratio and a greater amount of absorption in the δ 1.0-3.0 region in the $^1$H-NMR, and it is an item of some interest as to whether these variations arise from differences in the lignin type or in the amount or binding of the carbohydrate material present.

The original lignins (prior to hydrothermolysis) showed a 3:1 ratio of $C_{Ar}:C_{MeO}$ and 2:1 for $C_{Ar}$ relative to the δ 60-90 ppm region. These results are consistent with the preponderance of the basic syringyl unit in the starting lignin, as the $C_\alpha$, $C_\beta$ and $C_\gamma$ carbons have been assigned as δ 88-90, 72-75 and 60 ppm, respectively[27].



The increase in the integration of the $^{13}$C-NMR absorption between δ 100-140 ppm relative to the $C_{MeO}$ absorption at δ 54-56 ppm is plausibly assigned to elimination reactions of syringyl units in the original lignin to give cinnamyl units (b). Thus the new olefinic carbons would contribute to the δ 100-140 absorption and, although the new olefinic hydrogens could not be positively confirmed in the $^1$H-NMR, these would be of low intensity and partially overlapping with the aryl and phenolic hydroxylic protons.



b

Further evidence for the syringyl origin of b is the fact that Douglas fir, known to consist almost exclusively of guaiacyl lignin, forms very little of this material. The products b are evidently rather inert to further reaction, as treatment of this fraction under our original rapid hydrothermolysis conditions resulted in the recovery of 80% of unchanged material and 20% conversion to material soluble only in acetone.

## Acetone-Only-Soluble Residues

Analysis by pyrolysis mass spectrometry[12a,28] of the residue from poplar sapwood gave peaks at m/z 69, 95, 96, 112 and 126 corresponding to those from the acetone-only-soluble residue from cellulose (previously assigned[28]) and low intensity peaks at m/z 154, 168, 182, 190, 194, 196 and 210 assigned[12a] to syringyl lignins, but extremely weak signals corresponding[12a] to guaiacols. However, the residues from poplar bark and heartwood gave strong peaks at m/z 124, 138, 152, 164, 166, 168, 272, 284, 298 and 312 that correspond to the peaks we observe from the corresponding residue from Douglas fir, and which have been previously assigned[12a] as arising from guaiacyl lignins. Thus it appears that the acetone-only-soluble residue from poplar sapwood is mostly cellulose derived, while the corresponding fractions from bark and heartwood are mainly lignin derived.

## Ether Solubles from the Aqueous Phases

Acetic acid and furfural and its derivatives were the major components of these fractions from all the constituents of poplar wood (Table 4). We have previously shown that cellulose leads to the furfural derivatives under these conditions[19], while neither cellulose nor lignin give appreciable yields of acetic acid. The small ether solubles from the aqueous phases resulting from the hydrothermolysis of isolated lignins almost exclusively consist of phenols. Hemicellulose is known[29] to be rich in O-acetyl groups, and evidently this forms the acetic acid by hydrolysis under the hydrothermolysis conditions.

TABLE 4

Compositional Analysis of Ether-Solubles from the Aqueous Phase*

| Substance | Sapwood | Heartwood | Bark | Douglas Fir |
|---|---|---|---|---|
| Acetic acid | 30 | 40 | 20 | 10 |
| Other aliphatic acids | 5 | 10 | 10 | 5 |
| Furfural | 30 | 10 | 12 | 10 |
| 5-Methylfurfural | 5 | 3 | 10 | 10 |
| 5-Hydroxymethylfurfural | 3 | 4 | 5 | 8 |
| Phenols (including guaiacol, syringol and alkyl derivatives) | 5 | 5 | 10 | 5 |
| Levulinic acid and lactones | 7 | 10 | 5 | 20 |
| Unidentified | 15 | 18 | 28 | 32 |

* figures represent wt.% of the aqueous phase ether-solubles

## Composition of the Lignin

In summary the $^{13}$C-NMR spectra of the isolated lignins from poplar sapwood and heartwood indicate a predominance of syringyl type structures and the chloroform-soluble oils derived from these lignins or the parent sapwood or heartwood are all similar and also show mainly syringyl type products by FTIR and $^{13}$C-NMR. The acetone-only soluble residues from poplar sapwood are shown by pyrolysis MS to be mainly carbohydrate derived material, while the poplar heartwood and bark and Douglas fir give product containing mainly guaiacyl type derivatives with some carbohydrate material also present in the heartwood derived material.

## Estimation of the Lignin Content in the Poplar Wood Regions

An estimate of the lignin present in the original wood can be made from the phenolic content of the products. For sapwood the ether-soluble oil yielded 8.6% of material identified as phenols, the chloroform-soluble oil gave 13.6% of sodium hydroxide-soluble material that is presumably phenolic, and the acetone-only-soluble residue can be crudely estimated as containing 2.4% phenols based on the assumption that the fraction of the total pyrolysis MS ion current assignable to phenolic fragments corresponds to the phenolic fraction in this residue. These total 24.6% and corresponding figures for heartwood are 4.0%, 10.8% and 9.9% (total 24.7%) and for the bark 8.7%, 2.0% and 16.0% (total 26.7%). These totals correspond very well to our Klason lignin determinations of 24.7% lignin for poplar sapwood and 25.2% for heartwood, and while it is not reasonable to expect such close agreement from this approximation, the results do indicate the value of the analysis of rapid hydro-thermolysis products for the characterization of different wood components, especially lignins.

## Correlation of Different Fractions from Hydrothermolysis With the Wood Components

Based on the reported[22] composition of P. deltoides (D-38) poplar clone of 24.2% lignin, 20.5% hemicellulose, 52.3% cellulose and 3.0 extractives, the contribution of the lignin and the cellulose to each of the product fractions from the poplar sapwood and heartwood can be calculated, as shown in Table 5. This calculation assumes that the separated components behave as they do in the wood itself, and that the proportion of lignin and cellulose is the same in both the sapwood and heartwood. There is some justification for these assumptions in our work as cited above and also in previous work.

The contributions expected from lignin and cellulose account for most of the observed products from the poplar sapwood and heartwood. Of the remaining balances, the extractives, 3% of the

## TABLE 5

Contributions to Poplar Sapwood and Heartwood Fractions Based on 21% Hemicellulose, 24% Lignin, 52% Cellulose and 3% Extractives

| Substrate | ASO | ESO | CSO | AOSO | APES |
|---|---|---|---|---|---|
| POPLAR SAPWOOD | | | | | |
| Whole Sapwood | 43.0 | 13.0 | 17.0 | 12.0 | 10.0 |
| Contribution from lignin | 21.1 | 6.7 | 13.7 | 0.7 | 0.7 |
| Contribution of cellulose | 15.6 | tr | 5.7 | 9.9 | 7.8 |
| Extractives | | 3.0 | | | |
| POPLAR HEARTWOOD | | | | | |
| Whole Heartwood | 48.0 | 7.0 | 18.0 | 33.0 | 12.0 |
| Contribution from lignin | 16.8 | 3.5 | 10.0 | 3.0 | 0.8 |
| Contribution of cellulose | 15.6 | tr | 5.7 | 9.9 | 7.8 |
| Extractives | | 3.0 | | | |

(All figures represent percentage of substrate as adjusted to the percentage of substrate in wood)

ASO = Acetone-soluble oil

ESO = Ether-soluble oil

CSO = Chloroform-soluble oil

AOSO = Acetone-only-soluble oil

APES = Aqueous Phase Ether-solubles

total, were argued above to appear in the neutral ether-soluble oil, and the hemicellulose contributed to the aqueous phase ether-solubles, particularly as acetic acid. The only significant product unaccounted for is some of the acetone-only-soluble residue from the poplar heartwood, which, as noted previously, was shown by pyrolysis MS to be mainly lignin derived. Thus it appears that some portion of the lignin in heartwood is behaving differently in the whole wood and the extracted lignin (including enzyme treatment in its isolation), perhaps because of undergoing some chemical modification during the lignin isolation, so that the material is not contained in the isolated lignin, or possesses enhanced reactivity , so that it does not contribute to the acetone-only soluble residue.

## CONCLUSION

Our studies on the rapid hydrothermolysis products from poplar wood, isolated lignins and cellulose provide an insight into the behaviour of the individual components of wood towards this wood conversion process and their contribution to the total product. The rapid hydrothermolysis process also provides an empirical means of lignin estimation in wood as well as an insight into the structure of this wood component.

## EXPERIMENTAL

Poplar wood (D-38 clone, P. deltoides, supplied by the Ontario Ministry of Natural Resources Laboratories) of about five years' age was separated into the bark, sapwood and heartwood by clearly visible colour demarcations. Each of these parts was cut into sticks of about 5 cm length and 0.5 cm width and air dried for 48 hours.

### Rapid Hydrothermolysis Procedure

About 1 g of the substrate (the appropriate morphological region of D-38 poplar wood or whole wood from Douglas fir or lignin) was placed in a stainless steel tubular reactor[15]. Distilled water (5 ml) was added, and nitrogen flushed through the system two or three times, after which the reactor was sealed and dipped into a pre-heated sand bath maintained at the desired temperature (about 350°C). As soon as the reactor contents attained the desired temperature (about 2 minutes) as indicated by a thermocouple attachment, the reactor was removed from the sand bath and dipped into cold water to quench the reaction. The gases were vented and the aqueous phase decanted off. The residue was treated several times with acetone, and the extract filtered on a sintered funnel to remove suspended solids. The clear filtrate was rotoevaporated to remove the acetone, and the residual oil weighed to obtain percentage conversion of wood. The aqueous and oil phases were pooled from a total of five runs for each substrate.

## Work-up of the Oil and Aqueous Phases

The aqueous phase was extracted thrice with ether (total 100 ml), the organic layer dried ($MgSO_4$) and concentrated. The residue was weighed and subjected to chromatographic and spectroscopic analysis.

The acetone-soluble total oil phase was initially treated with ether to obtain the ether-soluble oil fraction and ether-insoluble residue. This ether-insoluble residue was then treated with chloroform (50 ml) and again the soluble and insoluble fractions separated. The ether-soluble and chloroform-soluble oil fractions were independently analysed by FTIR, $^1H$ and $^{13}C$-NMR. The details of instrumentation were described earlier[20].

The ether-soluble oil was fractionated further into sodium bicarbonate-solubles and sodium hydroxide-solubles in that order and the residual material recovered from ether. This last fraction, insoluble in the bases, was classified as the neutral fraction, and extraction of this material in ether with hydrochloric acid (6N) did not show the presence of any basic product in the acid layer. Each of these three fractions ($NaHCO_3$ and NaOH-solubles and neutrals) were analysed by GC, EIMS and finally by GC/MS.

The chloroform-soluble oil was analysed by NMR and EIMS[20]. A portion of this fraction was treated with sodium hydroxide (1% aq) to determine the amount of material soluble in this reagent.

The residue from the ether and chloroform extractions (the acetone-only-soluble fraction) was a dark brownish solid not melting up to 350°C. It was also totally soluble in dioxane and tetrahydrofuran. Its FTIR was measured in nujol and pyrolysis mass spectrum recorded (for instrumentation details, see reference 30).

## Isolation of the Lignins from Poplar Sapwood and Heartwood

The appropriate wood was subjected to the Bjorkman procedure[31] to remove extractives. The residual wood was ball milled and then extracted with dioxane-water (9:1). The residue from this solvent was washed with distilled water, suspended in an acetic acid buffer (pH 4.6) and hydrolysed at 55°C with cellulase enzyme (supplied by Van Waters and Rogers Ltd., Toronto) for 72 hours in a Precision Scientific Orbital Shaker water bath. Fresh enzyme solution was added, and the hydrolysis continued for a further 72 hours. This mixture was centrifuged, the solid residue extracted with dioxane-water (9:1) repeatedly, and the dioxane-soluble lignin was recovered by concentrating the solvent. The crude lignin was dissolved in 90% acetic acid and precipitated into water. The precipitated lignin was filtered, washed several times with distilled water and finally freeze-dried.

## ACKNOWLEDGEMENTS

Financial support was provided by a Strategic Grant from the Natural Sciences and Engineering Research Council of Canada, by the Department of Energy, Mines and Resources (Canada) and by the Imperial Oil Company. The authors are grateful to Dr. R. J. Evans, SERI, Golden, Colorado, for running the pyrolysis mass spectra.

## REFERENCES

1. H. R. Bungay, Energy, the Biomass Options, Wiley, New York, 1981.

2. D. L. Wise, Bioconversion Systems, CRC Press, Boca Raton, 1984.

3. R. P. Overend, T. A. Milne and L. K. Mudge, Fundamentals of Thermochemical Biomass Conversion, Elsevier, London, 1984.

4. S. Hasnain, Fifth Canadian Bioenergy R & D Seminar, Elsevier, London, 1984.

5. P. Whiting and D. A. I. Goring, Wood Sci. Technol., 16, 261 (1982).

6. P. Chow, G. L. Rolge, C. S. Lee and T. A. White, In Proceedings of the IXth Cellulose Conference, J.Appl.Polym. Sci., Appl.Polym. Symposium 37, 557-578, Wiley, New York, 1983.

7. K. V. Sarkanen and C. H. Ludwig (eds.), Lignins: Occurrence, Formation, Structure and Reactions, Wiley, New York, 1971.

8. Y. Musha and D. A. I. Goring, Wood Sci. Technol., 9, 45 (1975).

9. T. Yamasaki, K. Hata, T. Kuguchi, Holzforschung, 32, 44 (1978).

10. T. Higuchi, M. Shimada, F. Nakatsubo and M. Tanahashi, Wood Sci. Technol., 11, 153 (1977).

11. C. Lapierre, H. J. Lallemand and B. Monties, Holzforschung, 36, 265 (1982).

12. (a) J. R. Obst, J. Wood Chem Technol., 3, 377 (1983).

    (b) J. R. Obst, Holzforschung, 36, 143 (1982).

    (c) J. R. Obst and J. Ralph, Holzforschung, 37, 297 (1983).

13. G. Bonn, R. Concin and O. Bobleter, Wood Sci. Technol., 17, 195 (1983).

14. C. J. Biermann, T. P. Schulz and G. D. McGinnis, J. Wood Chem. Technol., 4, 111 (1984).

15. D. Beckman and D. G. B. Boocock, Can.J.Chem.Eng., 61, 80 (1983).

16. O. Bobleter and R. Concin, Cell.Chem.Technol., 13, 583 (1979).

17. O. Bobleter, R. Niesner and M. Rohr, J.Appl.Polym.Sci., 20, 2083 (1976).

18. H. Robey, in Reference 4, p. 242; see also N. S. Thompson, Wood and Agricultural Residues: Res. Use, Feed, Fuels, Chem., Wood Agric. Residues, pp. 101-119, E. J. Soltes (ed.), Academic Press, New York, 1983.

19. R. K. M. R. Kallury, I. C. Ambidge, T. T. Tidwell, D. G. B. Boocock, F. A. Agblevor and D. J. Stewart, Carbohydr. Res., 158, 253 (1986).

20. D. G. B. Boocock, R. K. M. R. Kallury and T. T. Tidwell, Anal. Chem., 55, 1689 (1983).

21. E. Chornet and R. P. Overend, In Reference 3, p. 967.

22. D. Beckman, "International Energy Agency (IEA) Co-operative Project D-1 - Biomass Liquefaction Test Facility Project, Final Report", Vol. 3, p. 4 (1983).

23. R. Concin, P. Burtscher, E. Burtscher and O. Bobleter, Int. J. Mass Spectrom. Ion Phys., 48, 63 (1983).

24. E. Sjostrom, Wood Chemistry: Fundamentals and Applications, Academic Press, New York, 1981.

25. H. Budzikiewicz, C. Djerassi and D. H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, Amsterdam, 1967.

26. H. H. Nimz, U. Tschirner, M. Stahle, R. Lehmann and M. Schlosser, J. Wood Chem. Technol., 4, 265 (1984).

27. H. H. Nimz, M. Nemr, P. Schmidt, C. Margot, B. Schaub and M. Schlosser, J. Wood Chem. Technol., 2, 371 (1982); see also Reference 26.

28. H. R. Schulten, U. Bahr and W. Gortz, J. Anal. Appl. Pyrolysis, 3, 229 (1982).

29. See Reference 24, p. 65.

30. T. A. Milne and M. Soltys, J. Anal. Appl. Pyrolysis, 5, 111 (1983).

31. A. Bjorkman, Svensk Papperstidning, 59, 477 (1956).