

# The Role of Extractives During Vacuum Pyrolysis of Wood

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## Synopsis

Vacuum pyrolysis of wood, extractive-free wood, holocellulose, and Avicel was conducted and their oil yields were compared. Formic and acetic acids and levoglucosan contents of all the oil products were determined. Molecular beam mass spectrometry analysis of wood and extractive-free wood and their pyrolysis oils was performed. CO<sub>2</sub> and CO, the main pyrolysis gases, were measured for each pyrolysis experiment. The role of extractives and the modification in wood cellulosic structure, which occurred during wood extraction treatment process, were investigated. Extractives, lignin, and orientation of the cellulosic fibers all significantly influenced the production of pyrolysis oils and formic acid. Lignin and extractives exhibited an inhibiting effect for the production of acetic acid and levoglucosan, respectively. CO<sub>2</sub> and CO yields were affected by the presence of extractives and by the cellulosic fiber orientation.

## INTRODUCTION

It is known that factors like temperature, residence time, heating rate, pressure, particle size, secondary cracking, and the presence of catalysts or additives influence thermal decomposition reactions.<sup>1-4</sup> There is, however, a controversy whether pyrolysis of a given biomass material is simply the sum of pyrolytic properties of its individual components.<sup>5-18</sup> The main object of this study was to investigate the properties of wood components, and extractives in particular, when pyrolysis was conducted under vacuum. The approach used involved separation of the extractives (also called "secondary constituents") followed by pyrolysis of the extractive-free wood material. The influence of extractives and the other constituents was studied by comparing the behavior of wood and extractive-free wood during pyrolysis.

Very few studies have been done on the role of wood extractives during pyrolysis. One reason might be that extractives are a minor wood constituent. Extractives as a class of wood components usually represent between 5 and 10% by weight of the dry biomass. They include volatile oils, terpenes, fatty acids, sterols, tannins, flavonoids, waxes, resins, coloring matters, and gums. Petroff and Doat<sup>7</sup> carbonized three kinds of wood with a varying extractive content. Pyrolysis was performed on 50- to 120-g samples under atmospheric argon pressure. As the extractive content decreased, the pyrolysis oil yield increased accordingly, whereas cellulose content had reverse effect. Kryla<sup>19</sup> re-

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ported that the yield of wood char produced in between 250 and 600°C increased as the extractive content increased.

## EXPERIMENTAL

### Materials

#### *Biomass*

The wood feedstock used was a debarked 20-year-old fast growing aspen poplar (*Populus tremuloïdes*) from Eastern Townships in the province of Quebec. It was ground to 40/60 Tyler mesh, and its elemental analysis was 49.5% C, 6.2% H, 0.3% N, and 44.0% O. Its average moisture and ash content were 5.0 and 0.4%, respectively.

#### *Holocellulose*

The holocellulose fraction was produced by eliminating lignin from the extractive-free wood feedstock following the chlorite method.<sup>20</sup> Its humidity, ash, and residual lignin content were 5.3, 1, and 3.1%, respectively.

#### *Cellulose*

A commercial alpha-cellulose stock (Avicel) with 3.5% humidity was supplied by FMC with degree of polymerization of approximately 154 and trace quantity of ash.

### Extraction Procedure

The extractives were separated according to the ASTM D 1105-56 (1979) standard method or TAPPI T 12M-45 applicable to North American woods. According to this method, 12 g of wood sieved to 60/80 mesh were extracted in a soxhlet apparatus with predistilled ethanol-benzene (1 : 2 volume ratio) for 4 h and followed by ethanol extraction. The residue was air-dried overnight to eliminate the alcohol and then oven dried at 150°C for 2 h to achieve a constant weight. The wood sample was then extracted with distilled water at 100°C for 1 h. The latter extraction was repeated three times with fresh hot distilled water. The residue was washed again with 500 mL of distilled cold water and dried at 105°C for 2 h.

### Pyrolysis

Schematic view of the pyrolysis system is shown in Figure 1. The system comprised a bench scale, batch vacuum retort. The cylindrical stainless steel retort was equipped with an inner quartz liner to prevent catalytic effect of the hot metallic walls of the reactor. A 30-g air-dried sample with 40/80 mesh was transferred into the reactor at the beginning of a run. The total pressure in the system was maintained between 130 and 470 Pa. The reactor was heated at a rate of 10°C min<sup>-1</sup> and was kept at the final desired temperature for 30 min. The vapors with about 2-s residence time were rapidly pumped out of the reactor and condensed in a series of cold water and dry ice-acetone condensers. The

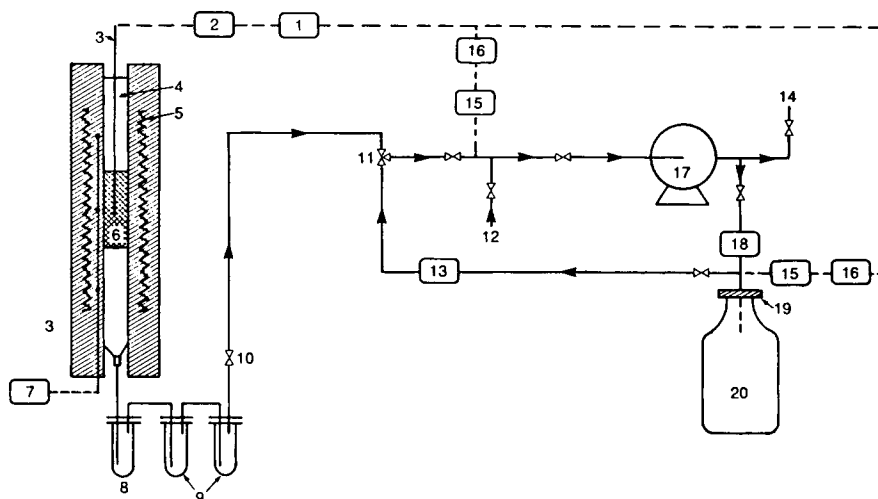


Fig. 1. Schematic view of the bench scale vacuum pyrolysis unit: 1, recorder; 2, thermocouple meter; 3, thermocouple; 4, retort; 5, three-zone electric furnace; 6, sample; 7, temperature programmer; 8, ice and water cooling trap; 9, dry ice-acetone cooling traps; 10, two-way valve; 11, three-way valve; 12, argon inlet; 13, gas analysis unit; 14, vent; 15, electronic manometer; 16, digital readout; 17, vacuum pump; 18, mist oil decanter; 19, vacuum seal; 20, gas collecting bottle.

noncondensable gases were evacuated and stored in glass bottles at room temperature. The solid residue was left behind in the retort. At the end of each run, the reactor was cooled down to room temperature and then argon was introduced into the reactor in order to prevent any possible oxidization during product recovery. The pyrolysis oils were recovered in tetrahydrofuran (THF) and subjected to various tests, which are described next.

### Analytical Methods

A series of analyses were carried out on the liquid phase including determination of carboxylic acids, sugars, and water. The  $C_1$  to  $C_7$  carboxylic acids of the wood pyrolysis oils were analyzed by gas chromatography following their conversion into benzyl esters via tetrabutylammonium salts and purification by solvent extraction and silica gel elution chromatography.<sup>21</sup> Sugar analysis and hydrolysis were performed following the silylation method.<sup>22</sup> Water was determined following the Karl Fischer method.<sup>23</sup> Elemental analysis of the solid residue was based on the standard ASTM D3176-74 method. Volatile matter was measured by ASTM D3175-82 method. The noncondensable pyrolysis gases were analyzed by gas chromatography.<sup>24</sup> Other details regarding the experimental method used will be found elsewhere.<sup>25</sup>

## RESULTS AND DISCUSSION

Chemical composition of a wood species varies with respect to location and age of the sample tree. Moreover, the chemical composition of one particular tree will significantly vary when sampling is made from different parts of the

tree. Chemical composition of the wood feedstock sample used (*P. tremuloides*) as average values of at least three tests is shown in Table I.

X-ray analysis of the extractive-free wood (0.3% ash and 6% moisture) showed a modified ash composition with respect to wood feedstock. Molecular beam mass spectrometry analysis<sup>26</sup> of the same sample showed on the other hand no significant alteration in its lignin and carbohydrate content after removal of the extractives. X-ray analysis of the holocellulose and wood ash was also performed. The former only showed a difference in high chlorine content (due to the technique of holocellulose extraction) with no other modification.

Pyrolysis of wood, extractive-free wood, Avicel, and holocellulose samples were performed at different temperatures as explained in the experimental section and showed satisfactory mass balances that ranged between 97 and 102%. The oil yields are shown in Figure 2. All pyrolysis oil products were analyzed for their formic and acetic acids and levoglucosan contents, as well as other sugars (galactose, glucose, mannose, arabinose, xylose, and ribose). The acid and sugar yields were compared in order to shed light on the role of extractives in wood decomposition mechanism. The sugar and acid yields as a function of wood decomposition temperature are illustrated in Figures 3–5. In Figures 2–5, the contribution of each single wood component was calculated as a function of its initial proportion in the original wood.

### Oil Yield Production

Wood decomposition reactions are significantly affected by various interactions existing in between their components, as illustrated in Figure 2. When examining the data for wood and extractive-free wood in particular, we concluded that extractive-free wood yielded higher amounts of oils than wood, as reported earlier by Petroff and Doat,<sup>7</sup> but higher amounts of charcoal (see Table II), in contradiction with Kryla's finding.<sup>19</sup> Figure 2 illustrates the variation of oil yields for wood, extractive-free wood, and holocellulose pyrolysis between 200 and 550°C. Figure 2 reveals the extractives unfavorable effect on oil yield, particularly for the range of temperatures between 250 and 350°C.

TABLE I  
Repetitive Analysis of Wood Feedstock Constituents

Analysis	Repetitive analysis (wt %) on dry wood basis			Corrected average values
	1	2	3	
Ash ASTM D 1102-56	0.3	0.4	0.4	0.4
Moisture, as-received basis ASTM E 203	—	—	—	—
Extractives ASTM D 1105-56	8.6	11.7	5.2	8.5
Holocellulose, as-received basis (chlorite method)	71.5	69.9	77.0	72.8
Lignin ASTM D 1106-56	19.6	18.0	17.4	18.3
Total	100	100	100	100

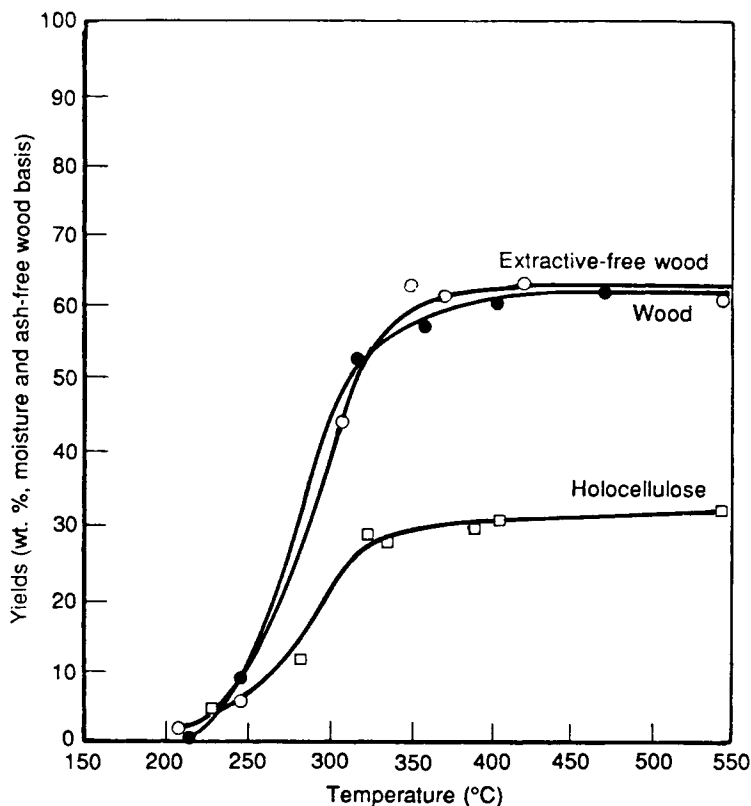


Fig. 2. Oil yield from wood, holocellulose, and extractive-free wood samples.

During the water and alcohol extraction of secondary constituents, wood structural polymer chains (mainly polysaccharides) are pushed apart as wood swells and cellulose fiber orientation changes. Such new orientation of the inflated cellulosic material together with the extractive removal apparently enhanced the oil yield within the pyrolysis temperature range of 250–350°C, which also corresponded to the cellulose decomposition temperature range. In order to further investigate this observation, wood was soaked in cold water, which resulted in a 0.9% weight reduction (due to the partial loss of some secondary constituents) of the dry material. The oil yield increased from 39.8 to 51.2% (wt %, dry wood basis) for the soaked material.<sup>27</sup> This finding supported the hypothesis of cellulosic fiber orientation and inflation leading to higher oil yields, which is in close agreement with Buch and Lewin findings.<sup>28</sup> In Figure 2, holocellulose yielded the least quantity of pyrolysis oils. Therefore, in addition to the fiber orientation effect, we concluded that lignin also positively enhanced the wood oil production.

### Carboxylic Acid Production

Extractives possibly acted as pyrolysis oil inhibitors, but their removal resulted in a significant reduction in formic and acetic acid yields (Fig. 3 and 4). Cellulose and hemicellulose are reported as the major sources of formic acid

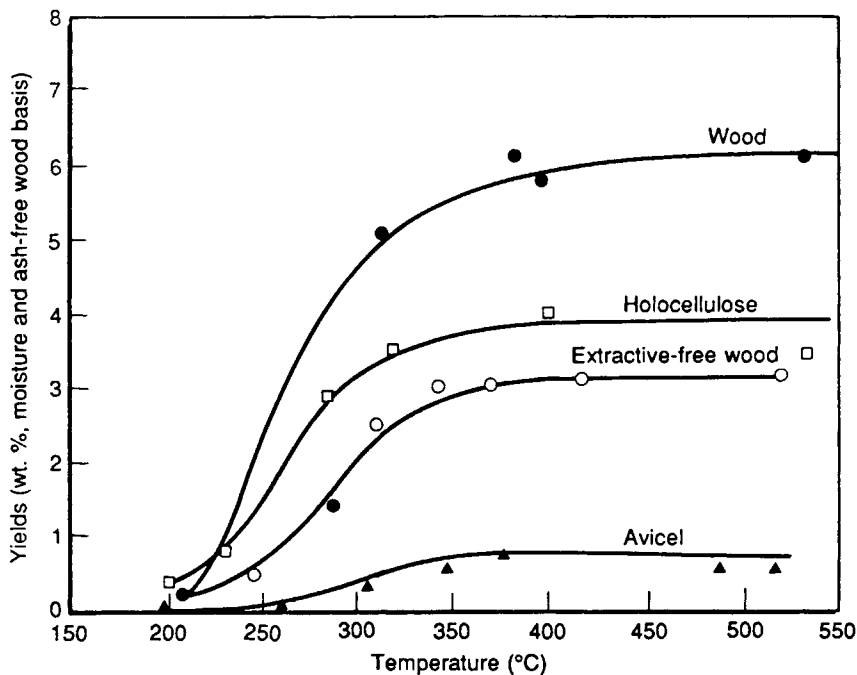


Fig. 3. Yield of formic acid from wood, holocellulose, extractive-free wood, and Avicel samples.

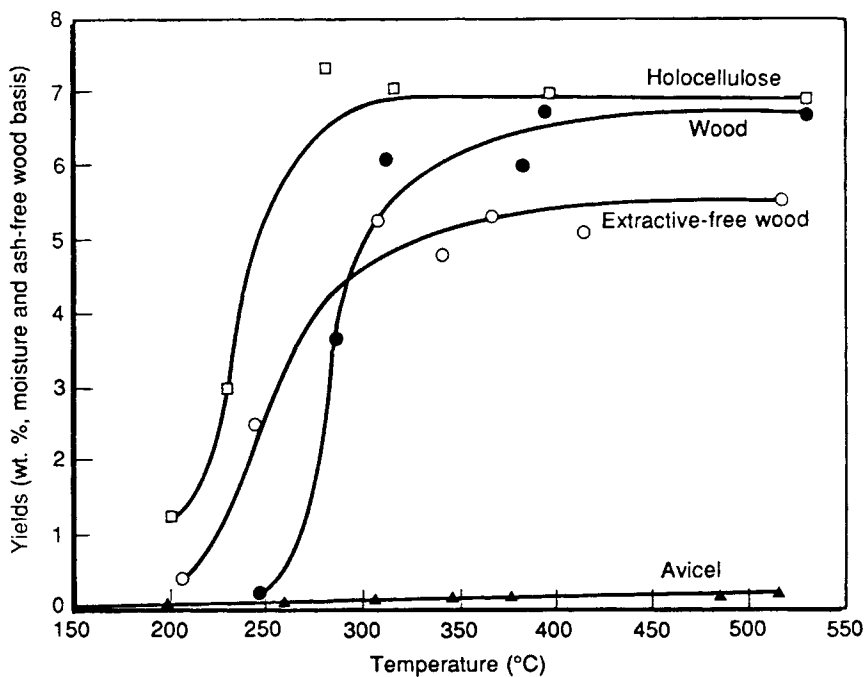


Fig. 4. Yield of acetic acid from wood, holocellulose, extractive-free wood, and Avicel samples.

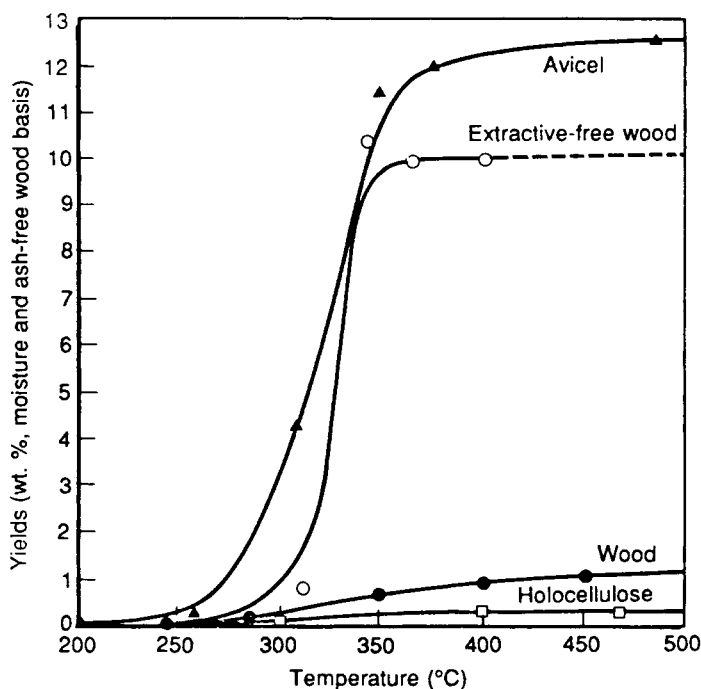


Fig. 5. Yield of levoglucosan from wood, holocellulose, extractive-free wood, and Avicel samples.

and acetic acid, respectively.<sup>29,30</sup> Since cellulose can hardly be separated from wood in the laboratory without structural modification, Avicel was used as a substitute, and it was pyrolyzed at different temperatures in the 200–530°C range (Fig. 3 and 4). Formic acid production from Avicel pyrolysis is shown in Figure 4. Apparently the low formic acid yield of Avicel compared to the original wood feedstock can be attributed to a *positive effect* of wood extractives. However, pyrolysis of the holocellulose portion of the investigated wood sample gave much higher yields of formic acid than Avicel alone but less than the original wood. Certainly the original wood cellulose has a considerable difference in its chemical structure compared to Avicel. We postulated that the difference between formic acid yields from holocellulose and Avicel in Figure 3 is mainly related to the difference in their cellulosic structure. It is also possible that the lower formic acid production of holocellulose compared to the initial wood is partially due to the cellulose structural alterations, its crystallinity in particular,

TABLE II  
Yield (wt %) of Pyrolysis Products Obtained at 540°C

Material	Oil	Charcoal	Water	Gas
Wood	60.7	14.4	14.1	10.8
Extractive-free wood	68.0	16.5	10.1	5.5

during the extraction procedure. Whether extractives have any positive effect on formic acid production in the initial wood cannot be postulated unambiguously at this stage, but indeed they are not the main source of formic acid nor acetic acid. Finally, the small difference in the formic acid yield between holocellulose and extractive-free wood material (approx. 0.8%) can be attributed to the inhibiting effect of lignin at this stage.

Acetic acid was produced at slightly higher yield from holocellulose and at significantly lower yield from the extractive-free wood compared to the original wood (Fig. 4). Avicel on the other hand produced trace quantities of acetic acid. There are three factors that influence acetic acid production: lignin, extractives, and hemicellulose fiber orientation (structure modification). Since hemicellulose has a less ordered structure with a smaller number of sugar residues per molecule (100–200) compared to cellulose, any structural modification is less likely to have a significant effect on the acetic acid production. According to Figure 4 removal of extractives resulted in a 1.2% decrease in the acetic acid yield, which approximately corresponded to 3.7% loss in hemicellulose during the water treatment. Indeed hemicellulose is known to be highly soluble in water. In this experiment, however, we have not measured the hemicellulose solubility in water during wood treatment. Therefore we were unable to conclude whether extractives have positive or negative effect on acetic acid production. Similarly we were unable to confirm any contribution of the hemicellulose structure modification on the acetic acid production. The difference in the acetic acid yield between holocellulose and extractive-free wood (approx. 1.4%, Fig. 4) can be mainly attributed to the inhibiting effect of lignin at this stage.

A final observation on Figure 4 is that both holocellulose and extractive-free wood yielded acetic acid at a temperature as low as 200°C in contrast to 250°C for wood. Retardation in acetic acid production also positively revealed the inhibiting role of lignin during the early course of wood thermal conversion.

### Sugar Production

For further progress of our study, we measured the levoglucosan content of wood, extractive-free wood, Avicel, and holocellulose pyrolysis oils at different decomposition temperatures. As illustrated in Figure 5, Avicel is the major source of levoglucosan. The extractive-free wood material produced about 10 times more levoglucosan than the original wood, which is supporting the inhibiting effect of extractives. Holocellulose pyrolysis oil on the other hand yielded surprisingly the least amount of levoglucosan, which may eliminate any positive contribution of wood structural modification during the water treatment on levoglucosan production. The respective role of extractives, lignin, and residual chlorine (in holocellulose) on the yield of levoglucosan has not been clarified at this stage.

Earlier we mentioned that wood and extractive-free wood exhibited two similar mass spectrometric fragmentation patterns that were recorded on molecular beam sampling mass spectrometer by Milne at SERI.<sup>26</sup> Their pyrolysis oils on the other hand exhibited two rather different fragmentograms (Fig. 6). If we compare the 124/126 fragment ion peaks ratio ( $m/e$  124 and 126 are the characteristic fragments of lignin and cellulose, respectively) in the two spectra, the carbohydrate content of the wood pyrolysis oil will be found lower than the



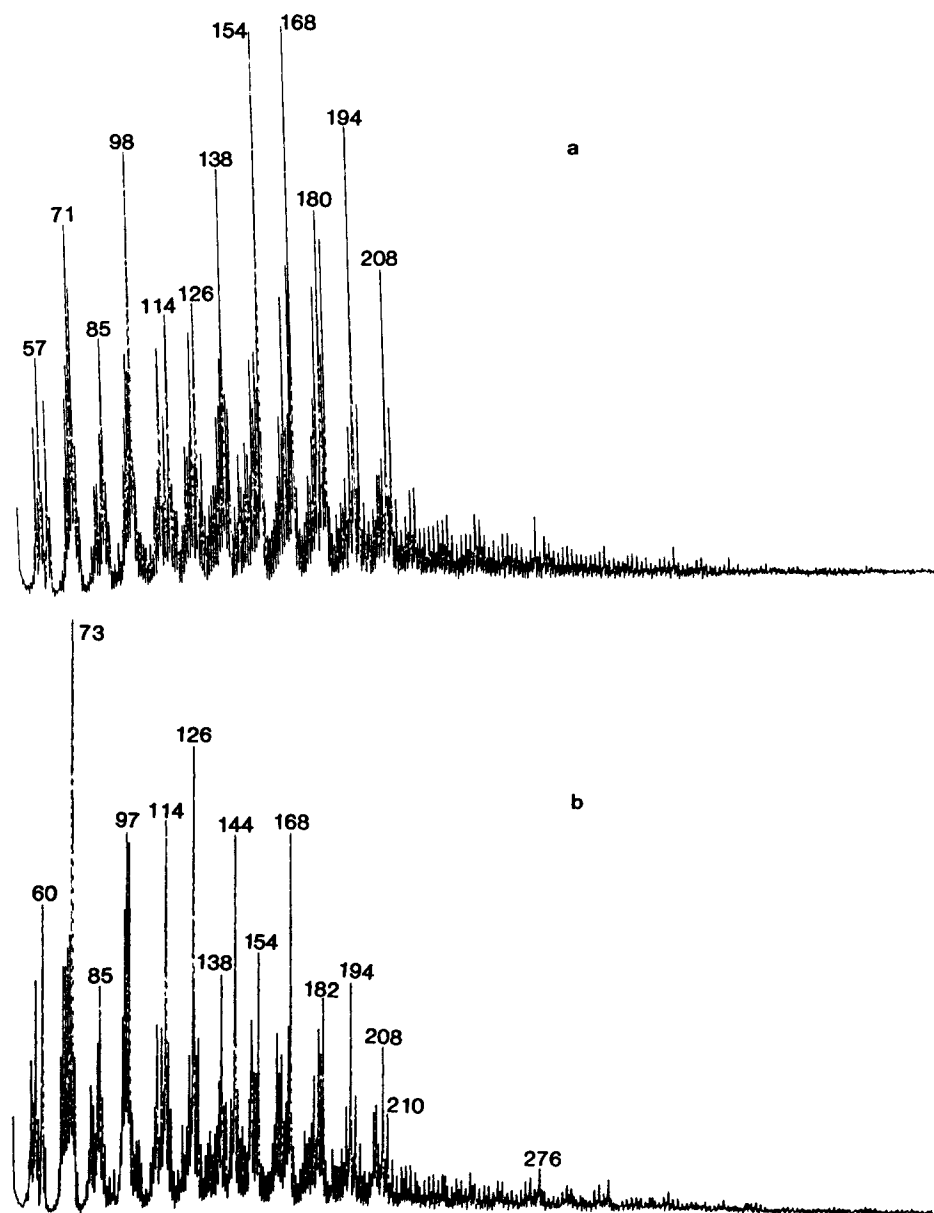


Fig. 6. Mass spectra of wood oil (a) and extractive-free wood vacuum pyrolysis oil (b).

carbohydrate content of extractive-free oil (Fig. 6 (a) and (b), respectively). Similarly, the  $m/e$  144 and 73 fragment ion peaks, which are typical levoglucosan characteristic peaks, are in greater proportion in the extractive-free wood pyrolysis oil than in the initial wood pyrolysis oil.

As briefly mentioned earlier, we have conducted another experiment by pyrolyzing 635 g of wood and wood treated with distilled water (wood was soaked in cold water for 48 h and then air-dried). The pyrolysis heating rate was  $1^{\circ}\text{C min}^{-1}$  up to  $450^{\circ}\text{C}$ . Levoglucosan content of soaked wood pyrolysis oils was

found to be several times higher than the initial wood oil. Under similar pyrolysis conditions, Shafizadeh,<sup>31</sup> concluded that an increase in levoglucosan production may be due to the elimination of inorganic impurities during the cold water soaking process, increase in surface activity by inflation of wood fibers, and change in degree of cellulose crystallinity. According to this study, it seems also that extractives are detrimental to levoglucosan production under pyrolysis conditions.

We think extractive-free wood with its reoriented cellulosic fibers is subjected to a rather different pyrolysis pathway, presumably an intermediate step, compared to the initial nontreated wood, which tends to increase the sugar yield. Whether the composition of wood extractives have any significant effect on pyrolysis mechanism and pyrolysis oil composition has not been studied yet.

### Solid Residue and Gas Production

We have established an empirical formula of  $C_6H_{3.2}O_{1.6}$  for the wood charcoal residue produced at  $400^\circ\text{C}$ , which is in a close agreement with Shafizadeh.<sup>32</sup> The empirical formula for the extractive-free wood charcoal on the other hand was  $C_6H_{2.2}O_{0.5}$ , interestingly revealing a reduction of approximately 34 and 64% in their hydrogen and oxygen contents, respectively. A study of the influence of extractives on the composition of wood charcoal samples produced during vacuum pyrolysis of *P. tremuloïdes* was recently conducted using the newly developed ESCA technique.<sup>33</sup> It has been proposed that the heat-resistant ex-

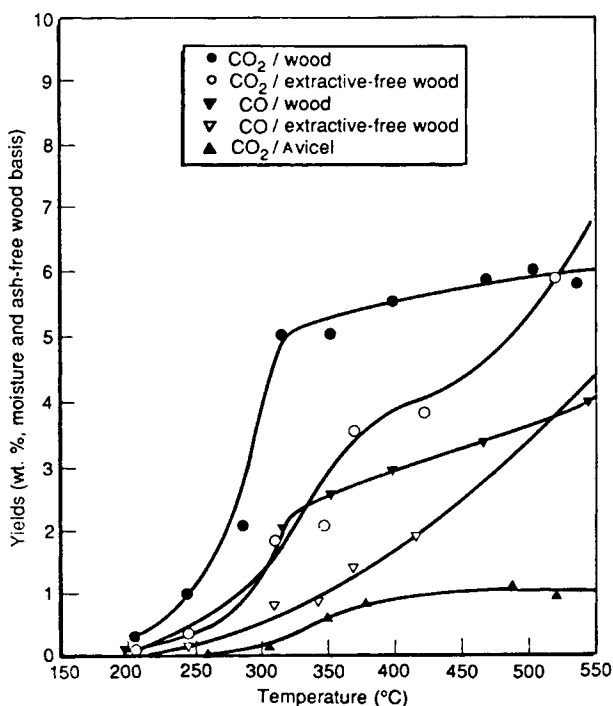


Fig. 7. Yield of primary noncondensable gases from wood, extractive-free wood, and Avicel samples.

TABLE III  
Effect of Extractives, Lignin, and Cellulosic Structure on Some Pyrolysis Product Yields<sup>a</sup>

Variable	Oil	Formic acid	Acetic acid	Levoglucosan	Gas
Extractives	–	+ (?)	?	–	Yes
Lignin	+	–	–	?	?
Cellulosic fiber orientation	Yes	Yes	No	?	Yes

<sup>a</sup> – negative effect, + positive effect.

tractives that cover the middle lamella surface during pyrolysis may behave as mass transfer barrier.<sup>34</sup> This phenomenon would explain the significant increase in oil yield after removal of extractives prior to pyrolysis.

With respect to pyrolysis gas composition, we found that carbon monoxide, carbon dioxide, and methane were the major pyrolysis gases produced at 500°C during pyrolysis of either wood or extractive-free wood materials. Figure 7 shows as an example the evolution of CO and CO<sub>2</sub> yields at different temperatures based on the initial wood organic matter. Figure 7 also indicates a smoother CO and CO<sub>2</sub> production rate for the extractive-free wood compared to the original wood feedstock. Between 200 and 350°C, the rate of gas production was fast and then leveled off for wood, whereas for the extractive-free wood, the rate was rather constant particularly for CO, which is indicative of wood extractive retardation effect during gas production. This indicated, in addition, that any divergence from the original wood cellulosic structure tended to significantly alter its pyrolysis gas production rate.

Influence of wood extractives, lignin, and cellulose fiber orientation during water treatment are summarized in Table III.

## CONCLUSION

Wood extractives exhibited a significant inhibiting effect on hard wood vacuum pyrolysis oil yield. Wood cellulose was found to be the main source of formic acid when it was pyrolyzed in the presence of extractives. Extractives inhibited levoglucosan formation during vacuum pyrolysis of lignocellulosic materials. Nevertheless wood cellulose was found to be a less favorable source for levoglucosan compared to Avicel, a crystalline cellulose.

Removal of extractives did not appear to significantly modify the hemicellulose composition, as reflected by the similar yields of acetic acid derived from wood and extractive-free wood material. Lignin was found to inhibit the carboxylic acid production and enhanced the oil yield. Approximately 50°C retardation was found in the acetic acid production temperature range (i.e. 250–350°C) as extractives were removed. Removal of wood extractives resulted in about 34 and 64% loss in hydrogen and oxygen content, respectively, of the pyrolysis solid residues. Extractives had also approximately 50°C retardation effect on gas production.

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