

CHEMICAL CHARACTERIZATION OF WOOD OILS OBTAINED IN A VACUUM PYROLYSIS PROCESS DEVELOPMENT UNIT. Hooshang Pakdel\* and Christian Roy\*\*,\*\*

\* Université Laval  
Chemical Engineering Department  
Pavillon Adrien-Pouliot  
Sainte-Foy (Québec) G1K 7P4

\*\* Assistant Professor at Université Laval and  
Adjunct Professor at Université de Sherbrooke

INTRODUCTION

The identification and extraction of valuable chemicals from wood-derived oils is a very important goal for the biomass thermochemical conversion industry (1,2). Pyrolysis oils have been extensively studied and several pure compounds that are found in wood oils have already been separated (3,4). However to our knowledge there are only two general methods which have been reported for the fractionation of pyrolysis oils into chemical groups: the solvent extraction method (5) and the adsorption-chromatographic method (6). The former technique is rather tedious and quite often the phase separation is difficult due to the emulsion formation. The yield of extraction strongly depends on the solvent volume and extraction repetition number. The adsorption-chromatography method was used for this investigation with further modifications which will be discussed later.

Extensive work conducted by different authors utilizing GC and GC/MS sometimes leads to different results, which indicates the difficulties of carrying out accurate detailed analyses of the chemical constituents of pyrolysis oils. Examples of incomplete or even contradictory results can be found in the literature (3,7) and this paper for the analysis of vacuum pyrolysis oils. Other researchers have studied functional group distribution in pyrolysis oil (8). Although those techniques are long and tedious, they will lead to useful information about wood oil chemistry.

The majority of compounds found in pyrolysis oils are oxygenated with rather similar polarity. Therefore their gas chromatograms in general suffer from low resolution and consequently the quantitative analysis will be less accurate. Although this problem may be partially obviated by choosing narrow bore and long capillary columns, but they are very expensive and not very practical. Direct injection of a complex mixture into the gas chromatograph on the other hand, tend to deteriorate the column by building-up of non volatile matter in the column inlet, leading to gradual decomposition of the column stationary phase. Generally gas chromatography has a limited application and is not meant to be used for very complex and less volatile mixtures. GC/MS is a much more powerful analytical tool but would not be available in a great majority of cases. Besides it is quite costly and requires skilled operators for the interpretation of the results. Therefore development of new methods of separation and fractionation in particular are needed.

The primary objective of this work is to develop a separation and fractionation method for better and detailed analysis of pyrolysis oils. This will eventually enable us to make correlations between the oil properties and pyrolysis operation conditions. Full characterization of the oils will also shed some light upon the possible pyrolysis reaction mechanism and the upgrading of the oils. The secondary objective is to develop methods for extraction of valuable chemicals such as specialty and rare chemicals which are in increasing demand (9).

## EXPERIMENTAL

The wood oil samples which have been characterized in this work have been obtained from pyrolysis of Populus deltoides (clone D-38) with no bark in a multiple-hearth vacuum pyrolysis reactor. The Process Development Unit (P.D.U.) has been described in detail by one of the co-authors in another paper (1).

The P.D.U. was tested for the production of high yields of oils from wood chips. One objective was to separate the bulk of the aqueous phase from the organic liquid phase by means of fractionation of the oil directly at the outlet of the reactor. This was achieved in the following way. The organic vapor product was removed from the reactor through six outlet manifolds which corresponded to the six heating plates of the reactor. The vapors were condensed in two condensing units named Primary and Secondary Condensing Units (P.C.U., S.C.U.). P.C.U. consisted of six heat exchangers in parallel and S.C.U. consisted of three traps placed in series. The pyrolysis oils which were obtained in both condensing units were subjected to sequential elution by solvent chromatography. The organic fractions were then analyzed as described below:

One gram of the oil sample was transferred into a glass column with 16 mm i.d. packed with 12.5 g of 60-200 mesh silica-gel in petroleum ether (30-60 °C b.p.). Fourteen fractions were collected, using different solvents as depicted in Table 1.

All the solvents were distilled before use and the silica-gel was washed with dichloromethane and dried in air. The other fractions were dried by rotary evaporator without heat. All the yields are shown in Table 1. FTNMR spectra of 5% solution in DMSO were recorded on XL 200 Varian instrument. Gas chromatographic analyses were performed on a 6000 Varian gas chromatograph with flame ionization detector and two injectors (on column and split). The capillary columns were J & W fused silica: DB5, 30 m X 0.25 mm i.d.; DB1, 30 m X 0.32 mm i.d. and DB1701, 30 m X 0.25 mm i.d. The results shown in this paper are on DB1 and DB5 columns. The carrier gas was He and N<sub>2</sub> as make up gas. The oven temperature was maintained at 50 °C for 2 min. then programmed to 150 °C and 290 °C at rates of 4 and 10 °C min<sup>-1</sup> respectively. Water's 840 data and chromatography control station with digital professional 350 computer and LA50 recorder were used as data processor.

Hydrolysis followed by sugar analysis was carried out according to the well know silylation technique. The procedure can be found elsewhere (10).

Gel permeation chromatographic (G.P.C.) analysis of the six oils from P.C.U. and one oil from S.C.U. (trap 1) were performed on ALC/GPC-201 Water's Associate liquid chromatograph equipped with a model R-401 refractometer. Four 30 cm X 7.8 mm i.d. columns packed with 100, 500, 10<sup>3</sup> and 10<sup>4</sup> μstyragel were used in series. The samples were prepared in THF (5%) and 15 μl were injected and eluted with THF. The following standards were used to calibrate the system: polystyrenes (M<sub>w</sub> = 4000; 2000; 800 and 600), polyethylene glycol (M<sub>w</sub> = 450, 300, 200), guaiacol, syringaldehyde and vanilline.

## RESULTS AND DISCUSSIONS

The pyrolytic products can be divided into four parts as below:

- 1- Light organic chemicals such as phenols which can be analyzed by conventional analytical techniques, mainly liquid and gas chromatography and mass spectrometry.
- 2- High molecular weight, less volatile and presumably more polar com-

pounds resulting from incomplete thermal degradation of lignin, cellulose and hemicellulose which can not be easily characterized (8).

3- Char

4- Gases (e.g. CO and CO<sub>2</sub>)

Part I will be discussed in this paper with appropriate references to Part 2 and 3.

The total oils from the six condensers (C<sub>1</sub> to C<sub>6</sub>) and an oil sample from Trap 1 (S.C.U.) were analyzed by GPC for their molecular weight range distribution. The average molecular weights for the condensers 1 to 6 were: 342, 528, 572, 393, 233 and 123 respectively. The test for Trap 1 showed an average molecular weight of about 100. The molecular weight distribution of Trap 1 was as below:

MW<100 (40%); 100<MW<200 (46.5%); 200<MW<300 (10.5%) and 300<MW<500 (3%).

The pyrolytic oil in S.C.U. contains about 38.8% of the total oil which consisted of 17.9% water and 5.6% carboxylic acids (11). Due to its average low molecular weight however, it is expected that the majority of the S.C.U. oil can be analyzed if the interference due to the water can be eliminated.

G.P.C. analysis was carried out for a series of pyrolytic oils obtained in a batch reactor operated at various temperatures similar to P.D.U. hearth temperatures (12). The results showed a rather similar average molecular weight which indicates a fair selective separation of wood oil constituents at various temperatures in P.D.U.

The results of silica-gel column fractionation of the oils (C<sub>1</sub> to C<sub>6</sub>) are shown in Table 1. The recoveries were approximately 4% higher probably due to the incomplete solvent removal. All fractions are designated as F1 to F14 in this part and all will be studied separately as shown in Table 1. F1 to F12 of all condensers were liquids with some differences in their colours and odors. The F13 and F14 were found to be very viscous and nearly solid. They became partially insoluble in water and methanol by redissolving them in water and methanol. F1 to F2 were not very soluble in methanol indicating their hydrocarbon nature. F4, 5, 6 showed some methanol insoluble matter which was identified as high molecular weight carboxylic acids in the range of C<sub>18</sub> to C<sub>30</sub> with a maximum at C<sub>24</sub> (11). These were separated and purified by crystallization in methanol. Although the high molecular weight carboxylic acids comprise very little percentage of the oil (~0.2%) but their finding is very interesting as only even carbon number acids up to C<sub>24</sub> have been already found in hardwood pyrolytic tar (13). The fractions 7 to 12 were slightly insoluble in dichloromethane and fully soluble in methanol. A preliminary composition analysis of each fraction was made and more work is in progress. The results are the followings:

#### Fraction 1:

This fraction mainly contains hydrocarbons with an odor typical of a fossil fuel mono-aromatic hydrocarbon. Proton nuclear magnetic resonance spectrum was recorded for a sample of C1-F1 (Condenser 1, Fraction 1) as an example and showed 4.5% aromatic, 2% olefinic, 18% methylenic hydrogens  $\alpha$  to the rings and 19.5%  $\beta$  to the ring and 56% methylene and methyl hydrogens further away from the ring. This distribution indicates long alkyl and alkenyl side chains on benzene rings. A significant difference was observed in their gas chromatograms from C1 to C6. C1 to C5 showed some similarities in a few well resolved peaks eluting out of the gas chromatographic column at above

200 °C. Recently a series of short side chain alkyl and alkenyl benzenes (up to C<sub>11</sub> H<sub>14</sub> & C<sub>11</sub> H<sub>16</sub>) were reported in wood pyrolysis oil (6). Condenser 6 on the other hand showed a broad range of hydrocarbons eluting above 100 °C. Materials eluting between 100 and 200 °C were rather less complex compared with the others eluting at above 200 °C. It is interesting to see in Table 1 that there is an increasing trend in quantity of the hydrocarbons up to the maximum in C<sub>3</sub> which falls down in C<sub>5</sub> and again reaches to the maximum at 18.5% in C<sub>6</sub>. Whether further increase of the hearth temperature will increase and produce any more materials has not been tested but we have made an infrared spectroscopic study of the solid residue which were left behind accidentally in each hearth after the run (14). Their infrared spectra is shown in Fig. 1. Despite of the fact that a bulk of the pyrolytic oils were produced in condensers 1 and 2 but there are very small changes which can be observed in H-1 (Hearth 1) and H-2 (Hearth 2) (see Fig. 1). However significant differences were observed for H-3 to H-6. Spectrum H-6 which was operated at 448 °C shows only minor bands due to the remaining organic matter, mainly lignin or recondensed materials (15). These materials were measured to be approximately 20% of the total residue.

#### Fraction 2

This fraction was in low abundance in all the condensers and their quantities are significantly dependent on the hearth temperature. Similar to Fraction 1, Condenser 6 showed a maximum quantity of Fraction 2. With a slight tailing from the earlier or later fractions, but the overall separation of Fractions 2 was good. Qualitative analysis of Fractions 2 by GC showed significant differences for Condenser 6 in particular. This Fraction is similar to Fraction 1 and has aromatic nature but more polar than Fraction 1. Its gas chromatogram showed well resolved peaks but their identification has not been completed yet. Condenser 5 & 6 have completely different composition from the rest. Their GC peaks are moderately resolved. It was interesting to observe a complete change in the distribution of the compounds by 50 °C change in the bed heating temperature from hearths 4 to 5.

#### Fractions 3 - 11

These fractions have a particular value as their constituents are valuable and many of them can be characterized by gas-chromatography. F3-11 contributed between 23 - 36% of the condensers oil and 40.5% of the total P.C.U. oil. The total yield of these fractions therefore can be used as quality index to compare different oils. This paper contributes to a small part of these fractions and further work is in progress.

Table 2 lists some of the compounds which have been analyzed in these fractions which are mainly mono phenolic types and oxygenated heterocyclic compounds. All the chromatograms of F3 to 10 showed well resolved peaks but F11 suffered from peak broadening which is more likely due to the contamination from F12. Examples of a few chromatograms are presented in Fig. 2 and are compared with a chromatogram of the total oil from condenser 6 (Fig. 2a). From Fig. 2a, we could only identify a few compounds and the rest were coeluting and masked with the other non resolved and broad peaks. Consequently, any quantitative analysis of the total oil will be incomplete and less accurate. Although the total materials listed in Table 2, apart from water, contribute to only 23% of the total dry oil in P.C.U. but they show an interesting distribution of the compounds in the different condensers which can be correlated with their source materials.

Characterization of the low molecular weight carboxylic acids which we have developed in our laboratory (11) enables us to observe a close agreement between our results and the generally accepted source materials for two

formic acid and acetic acids, i.e. cellulose and hemicellulose (16). The former as a source for formic acid decomposes at higher temperature than the latter which is the source for acetic acid. This was observed in the P.D.U. by comparing the acid yields in the condensers. Carboxylic acid characterization was successfully achieved by analyzing the oils before any fractionation.

Finding of acetol in relatively high abundance in Condensers 5 & 6 may indicate a lignin type source or decomposition of recondensed materials in hearths 5 & 6. Since a large number of five carbon atom sugars, the source material for furan derivatives, are associated with hemicellulose especially in hardwood (3) therefore their finding in Condenser 2 with maximum abundance gives more support to the selectivity of the separation in the P.D.U. system. Finding of phenol with high proportion in Condensers 1 to 3 and some in Condenser 6 is also interesting and supports the suggestion that cellulose is also a source for phenol during wood pyrolysis (3). Since no any significant quantity of phenol was detected in Condenser 5 but some in Condenser 6, the decomposition of recondensed materials in the hearth 6 is more likely to be the source of phenol in Condenser 6. On the other hand n-propyl phenol has been found in a relatively high percentage in Condenser 6 which indicates a different source, i.e. lignin for the substituted phenols. Although guaiacol, catechol, eugenol and isoeugenol are spreaded in all condensers with an increasing trend toward Condenser 6 therefore it may be true that their production starts as soon as lignin starts to degrade, presumably at 250 °C or even below. Earlier these compounds have been found in the tarry residue from lignin pyrolysis (17). p-Cresol which we have identified in Condenser 6 has been recognized to be a degradation product of the lignin (18), more likely at high temperature around 440 °C. Finding of higher proportion of aromatic hydrocarbons in Condenser 6 also indicates that lignin is a possible source for hydrocarbons.

#### Fraction 12

Under the gas chromatographic conditions used, we were unable to observe any well resolved peaks. Typically the chromatogram showed lots of unresolved broad peaks indicating its higher polarity than the previous fractions. Its pH value was also significantly lower than the other fractions. The proton FTNMR spectrum was recorded for the Fraction 12 of Condenser 1 and showed hydrogen distribution of: aliphatic (4%), cyclic methylenes or methylenes  $\alpha$ to the aromatic rings (20%), hydroxylic and methoxy groups (47%), olefinics and hydroxylics (17%), aromatics (8%), phenolics (3%) and aldehydics (1%). The total oil from Condenser 1 on the other hand showed: aliphatics (10%), cyclic methylenes or methylenes  $\alpha$ to the aromatic rings (31%), hydroxylics and methoxys (30%) olefinics and hydroxylics (7%), aromatics (16%), phenolics (4%) and aldehydics (2%). Comparison of these two spectra shows that the F12 has higher hydroxyl group than the initial oil. More work is in progress for further fractionation of this fraction.

#### Fraction 13

This fraction contains the highest percentage of the high polar compounds, oligosaccharides in particular. Two techniques of <sup>1</sup>H-FTNMR spectroscopy and hydrolysis were applied to further study of these fractions which are briefly discussed in this paper as follows:

NMR spectra were recorded for the oils from the condensers and their F13's and comparisons were made. Fig. 3a and 3b represent the NMR spectra of Condenser 6 and its F13 as an example. Both spectra were recorded in DMSO. All the samples were freely soluble in DMSO. The peak assignments were made as: aliphatic hydrogens (12%), cyclic methylenes or methylenes to the aromatic rings (38.5%), methoxys and hydroxylic groups (29.5%), olefinics

and hydroxylics (4%), aromatics (12%), phenolics (3%), and aldehydics (1%), and F13, contained 2, 14, 60, 15, 5.5, 2.5 and 1% respectively.

The hydroxyl group assignments were also confirmed by addition of a few drops of deuterium oxide before recording the spectrum. Consequently we observed that approximately 50% of the resonance bands in the range of 3-4.2 ppm are due to the sugars hydroxyl groups. Similarly approximately 30% of the resonance bands in the range of 4.2 - 5.5 ppm are also due to the hydroxyl groups. Their spectra have some similarities with the typical sugars NMR spectra. From their NMR spectra we observed an increasing trend to the high hydroxyl content from Condenser 1, F13 to Condenser 6, F13.

The hydrolysis experiments were carried out to measure the oligosaccharide content of the oils. Primarily analysis was made for the total sugar content of the oils following silylation technique. We found only levoglucosan with 0.3, 0.4, 0.7, 1.7, 3.4, and 4.2% in Condensers 1 to 6 respectively. This finding was in close agreement with the previous data obtained on a series of the oils obtained in batch reactor operating at a similar range of temperatures as P.D.U. Hydrolysis of the total oils were carried out and their sugar content were measured.  $\alpha$  and  $\beta$  Glucose and xylose were the most dominant sugars in hydrolysates. The total glucose content increased from Condenser 1 to 6 but xylose reached a maximum in Condenser 5 then decreased in Condenser 6. Their total sugar content were 3.14, 3.31, 6.85, 6.81, 14.23 and 14.05% for Condensers 1 to 6 respectively. Similar experiments were carried out on F13 for all Condensers. The results indicate that a complete recovery of levoglucosan was achieved in F13 but the hydrolysates showed approximately 30% loss. Further investigation is in progress to find the reason for this loss.

#### Fraction 14

This fraction comprised a small portion of the oils and a steady increase in their quantities was observed from Condenser 1 to 6. They may have presumably polymeric structure. Their infrared spectra showed a weak and broad hydroxyl stretching vibration band and very weak C=O and C-O absorption bands at 1700 and 1600 wavenumbers respectively. C-H stretching and vibration bands were also observed at very low intensities at 2920 and 1520 wavenumbers respectively.

#### CONCLUSION

The sequential elution chromatographic technique has been found particularly helpful in separating whole product oil produced by vacuum pyrolysis of wood into chemically distinguishable fractions. More than 30% of the P.C.U. oil that eluted first could be analyzed by GC and GC-MS with less unambiguity.

Now that sensitivity problems are being overcome, infrared spectroscopy and wet chemistry will be overtaken in some instances by high field  $^1\text{H-NMR}$ , a non destructive technique, and MS-MS spectroscopy and spectrometric techniques for characterization of the rest of the fractions namely F12, 13 and 14 in this investigation.

Fourier transform  $^{13}\text{C-NMR}$  which has not been utilized in this investigation is likely to make a large contribution also in the near future to study these fractions.

Since variation in the distribution of the separated fractions and their composition in different condensers were in good agreement with their generally accepted source materials, the P.D.U. is considered to be capable of selective separation of oils.

Even though they are only present in relatively low concentration, the compounds such as methyl cyclopentene-ol-one, 3- hydroxy - 2- methyl - 4- pyrone, isoeugenol and acetaldehyde, for example, can serve to characterize various oils and monitor the pyrolysis liquefaction procedure. They can also be separated and extracted as fine chemicals.

#### ACKNOWLEDGMENTS

This study was supported by Energy, Mines and Resources Canada (Ottawa).

#### REFERENCES

- 1- Lemieux, R., C. Roy, B. de Caumia and D. Blanchette. Preliminary Engineering Data For Scale up of a Biomass Vacuum Pyrolysis Reactor. Production Analysis and Upgrading of Oils from Biomass, ACS Symposium, Denver, Col. April. 5 - 10, 1987.
- 2- Perdrieux, S. La Valorisation chimique du bois par carbonisation. Le Bois National - 2 juillet, 23-26 (1983).
- 3- Soltes Ed. J. and T. J. Elder. Organic Chemicals from Biomass. I.S. Goldstein, ed. CRC Press. 63-99 (1981).
- 4- Elliott, D.C. Analysis and Upgrading of Biomass Liquefaction Products. Final Report, Biomass Liquefaction. Tests Facility, IEA, Co-Operative Project D-1, Jan. 10 (1984).
- 5- Boocock, D. G. B. and Sherman K.M. Further Aspects of Powdered Poplar Wood Liquefaction by Aqueous Pyrolysis. The Canadian Journal of Chemical Engineering. 63: 627-633. (1985).
- 6- Hubert, G.D., M.A. Eames, C. Figueroa, R.R. Gansley, L.L. Schaleger and D.W. Watt. The Products of Direct Liquefaction of Biomass. Fundamentals of Thermochemical Biomass Conversion. R.P. Overend, T.A. Milne and L.K. Mudge eds. Elsevier Applied Science Publication, London, New York. 1027-1037. (1984).
- 7- Ménard, H., D. Belanger, G. Chauvette, A. Gaboury, J. Khorami, M. Grisé, A. Martel, E. Potvin, C. Roy and R. Langlois. Characterization of Pyrolytic Liquids from Different Wood Conversion Products. Fifth Canadian Bioenergy R & D Seminar. S. Hasnain, ed. Elsevier Applied Science Publisher. 418-425. (1984).
- 8- Nicolaides, G.M. The Chemical Characterization of Pyrolytic Oils. Master Thesis. University of Waterloo. (1984).
- 9- Singh B.B. Strategic Options for Commodity Chemical Producers in Transition to Specialty Market Sectors. World Congress III of Chemical Engineering. Tokyo - Japan. Vol I: 23-26 (1986).
- 10- Ménard, H., M. Grisé, A. Martel, C. Roy and D. Belanger. Saccharification of Biomass by Pyrolysis at Reduced Pressure Followed by Hydrolysis. Fifth Canadian Bioenergy R & D Seminar. S. Hasnain, ed., Elsevier Applied Sciences Publisher. 440-444 (1984).
- 11- Pakdel, H. and C. Roy. Production and Characterization of The Low-Molecular-Weight Carboxylic Acids from Wood in a Vacuum Pyrolysis Process Development Unit. In preparation.

- 12- Brouillard, D. Role of Wood Constituents on Pyrolysis Reactions. M.Sc.A. Thesis. Université de Sherbrooke, Québec (1986). (In French).
- 13- Goos, A.W. The Thermal Decomposition of Wood. Wood Chemistry. L.E. Wise and E.C. Jahn, eds. Reinhold New-York, chap. 20, 826-851 (1952).
- 14- Roy, C., R. Lemieux, H. Pakdel, B. de Caumia and D. Blanchette. Heat and Mass Balance Around a Multiple-Hearth Furnace for Vacuum Pyrolysis of Biomass. World Congress III of Chemical Engineering, Tokyo, Japan, Vol. 1: 621-624 (1986).
- 15- Ahmed, A., J.L. Grandmaison and S. Kaliaguine. Characterization of the Solid Residues of the Supercritical Extraction of Populus Tremuloides in Methanol. Journal of Wood Chemistry and Technology. 6 (2), 219-248 (1986).
- 16- Shafizadeh, F., R.H. Furneaux, T.G. Cochran, J.P. Scholl, Y. Sakai. Production of Levoglucosan and Glucose from Pyrolysis of Cellulosic Materials. Journal of Applied Polymer Science. 23: 3525-3539 (1979).
- 17- Allan, G. G. and I. Mattila. High Energy Degradation. Lignin - Their Occurrence, Formation, Structure and Reaction. K.V. Sarkanen, C.H. Ludwig, eds. Chap. 14 (1971).
- 18- Fletcher, T.L. and E.E. Harris. Products from the destructive Distillation of Douglas-Fir Lignin, Tappi, 35: 536 (1952).

TABLE 1 - PRIMARY CONDENSING UNIT PYROLYTIC OILS AND THE YIELD OF VARIOUS CLASSES OF COMPOUNDS OBTAINED BY SILICA-GEL COLUMN CHROMATOGRAPHIC ANALYSIS (a)

SAMPLE	FRACTION	FRACTION	FRACTION	FRACTION	FRACTION	FRACTION	FRACTION	TOTAL
025-PHE-450-RL	1	2	3-11	12	13	14		
Condenser 1	1.2 (0.12)	1.3 (0.13)	315.7 (31.57)	282.8 (28.28)	311.1 (31.11)	10.8 (1.08)	923.0 (92.3)	
Condenser 2	3.9 (0.39)	0.4 (0.04)	364.2 (36.38)	363.8 (29.96)	283.1 (28.28)	20.1 (2.01)	971.7 (94.10)	
Condenser 3	14.7 (1.46)	1.2 (0.12)	238.7 (23.70)	302.6 (30.04)	321.6 (31.93)	29.4 (2.92)	908.2 (90.2)	
Condenser 4	12.3 (1.22)	0.0 (0)	265.3 (26.37)	346.1 (34.40)	316.0 (31.40)	30.0 (2.98)	969.7 (96.4)	
Condenser 5	2.9 (0.29)	0.5 (0.05)	239.4 (23.87)	338.9 (33.79)	331.3 (33.03)	36.2 (3.61)	949.2 (94.6)	
Condenser 6	18.5 (1.84)	8.9 (0.89)	357.4 (35.61)	285.3 (28.43)	308.7 (30.76)	44.9 (4.47)	1023.6 (102.0)	

(a) See the text for description of the classes.

All figures in parentheses are expressed in weight percentage (as-received oil basis). Otherwise, numbers are mg.

Fraction 1: 128 ml with petroleum ether  
 Fraction 2-11: 128 ml each with  $\text{CH}_2\text{Cl}_2$  / Petroleum ether mixture, from 10 to 100%  $\text{CH}_2\text{Cl}_2$  (10 % increments) for F2 to F11 respectively.  
 Fraction 12: 128 ml with ether  
 Fraction 13: 128 ml with water  
 Fraction 14: 60 ml with 10% formic acid in methanol

TABLE 2- PRELIMINARY ANALYTICAL DATA OBTAINED FROM PRIMARY CONDENSING UNIT

CC #	COMPOUND	CONDENSER 1	CONDENSER 2	CONDENSER 3	CONDENSER 4	CONDENSER 5	CONDENSER 6
---	Water	46.54 (8.24)	50.58 (6.8)	59.45 (6.24)	83.63 (6.54)	85.03 (6.60)	28.52 (5.12)
---	Formic acid	13.89 (2.46)	27.37 (3.68)	38.77 (4.07)	59.33 (4.64)	72.02 (5.59)	11.36 (2.04)
---	Acetic acid	40.50 (7.17)	58.83 (7.91)	62.40 (6.55)	40.15 (3.14)	31.82 (2.47)	9.64 (1.73)
1	Acetol	---	---	---	0.89 (0.07)	0.52 (0.04)	7.24 (1.3)
2	Furfural	0.28 (0.05)	0.37 (0.38)	0.44 (0.05)	6.52 (0.51)*	4.64 (0.36)	0.50 (0.09)
3	Furfuryl alcohol	1.58 (0.28)	2.75 (0.37)	14.3 (1.5)	---	---	2.45 (0.44)
4	Angellactone	0.68 (0.12)	2.90 (0.39)	0.48 (0.05)	0.02 (0.002)	---	---
5	Cyclohexanol	---	---	---	---	---	---
6	-Butyrolactone	---	---	---	---	---	4.79 (0.86)
9	Me-Cyclopentan-1-one	---	---	0.51 (0.05)	---	---	---
10	5-Me-furfural	---	---	1.05 (0.11)	1.92 (0.15)	---	1.28 (0.23)
11	Phenol	5.2 (0.92)	5.50 (0.74)	9.53 (1.0)	1.41 (0.16)	1.54 (0.12)	2.73 (0.49)
12	Me-Cyclopentane-ol-one	0.14 (0.02)	0.82 (0.11)	1.81 (0.19)	4.35 (0.34)	---	---
13	m-Cresol	---	0.28 (0.35)	---	---	---	0.56 (0.1)
13a	p-Cresol	---	---	---	---	0.64 (0.05)	4.07 (0.73)
14	Guaiacol	0.02 (0.003)	1.12 (0.15)	0.95 (0.1)	1.79 (0.14)	0.52 (0.04)	0.45 (0.08)
16	5-Hydroxy-2-Me-4-pyrone	0.51 (0.09)	0.59 (0.08)	---	---	---	0.67 (0.12)
18	Dimethyl 2,3, phenol	---	---	---	---	---	8.74 (1.57)
19	Dimethyl 2,5, phenol	---	---	---	---	---	3.34 (0.6)
19a	Di-propyl phenol	---	---	---	---	---	---
20	Hydroquinone	1.13 (0.2)	2.01 (0.27)	2.48 (0.26)	4.6 (0.25)	7.73 (0.6)	0.52 (0.04)
22	Resorcinol	---	---	---	---	0.52 (0.04)	8.35 (1.5)
23	Hydroquinone	---	---	---	---	5.02 (0.39)	0.45 (0.08)
24	Syringol	1.81 (0.69)	2.37 (0.5)	10.86 (1.14)	10.23 (0.8)	0.26 (0.02)	12.48 (2.24)
25	Eugenol	3.11 (0.02)	0.45 (0.06)	0.28 (0.03)	0.26 (0.02)	6.57 (0.51)	---
27	Isosuganol	3.22 (0.57)	3.05 (0.41)	6.29 (0.66)	5.37 (0.42)	0.13 (0.01)	---
28	Vanilline	---	---	---	---	---	---
	Sugars**	17.73 (3.14)	24.25 (3.26)	64.88 (6.81)	87.08 (6.81)	183.33 (14.23)	57.20 (14.05)
	Total	135.44 (23.98)	180.85(24.43)	273.48 (26.81)	306.76 (23.99)	431.97 (33.53)	173.56(31.16)
	Total in P.C.U. = 1502.06 (27.89) %	---	---	---	---	---	---

\* Could not be distinguished

\*\* Total sugars after hydrolysis

All figures in parentheses are expressed in weight percentage (as-received oil basis). Otherwise, numbers are g.

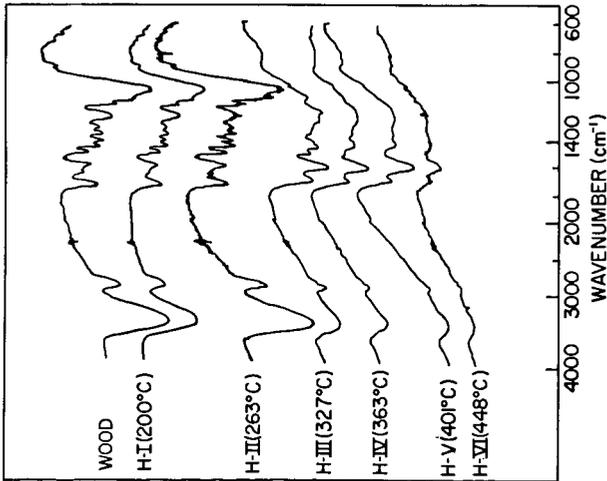


Fig. 1 - INFRARED SPECTRA OF WOOD AND SOLID RESIDUE. IN EACH SPECTRUM (INDICATED BY H.)

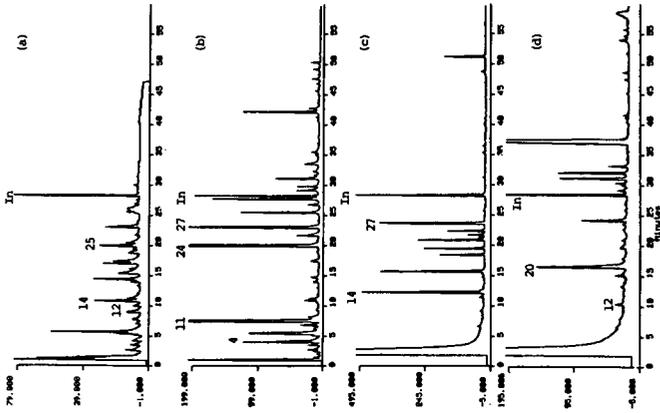


FIG. 2 - CAPILLARY GAS CHROMATOGRAMS OF: (a) total Condenser 6 oil; (b) Condenser 1 Fraction 1; (c) Condenser 2 Fraction 3 and (d) Condenser 3 Fraction 5. (See Table 2 for identification of peaks), In = Internal standard

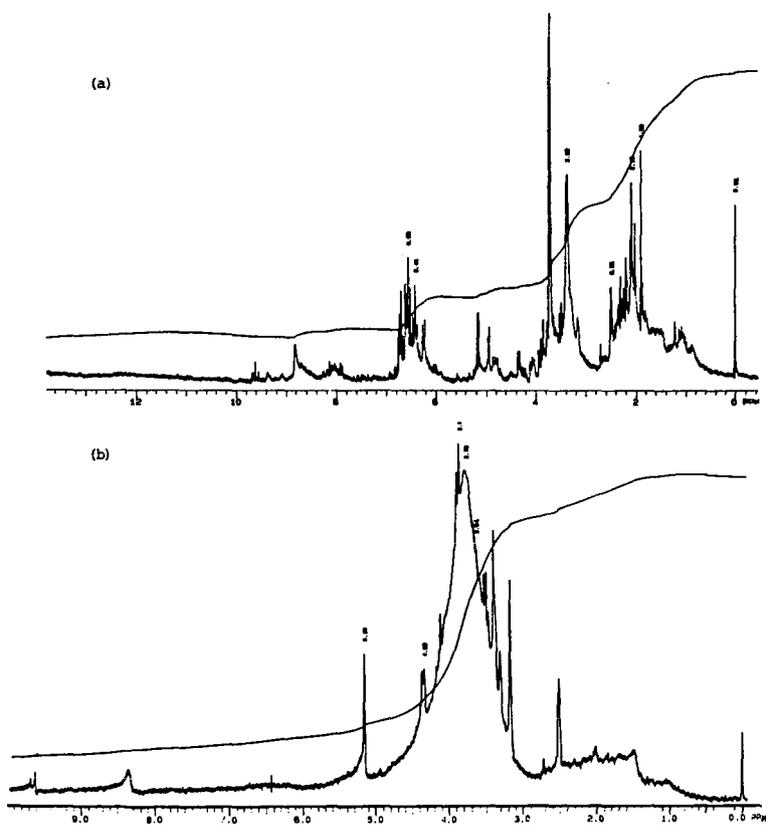


Fig. 3 - <sup>1</sup>H-NMR SPECTRA OF WOOD PYROLYTIC OILS  
 (a) Condenser 6; (b) Fraction 13 Condenser 6