

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 N₂ 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⁻¹ 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, 10³ and 10⁴ 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_w = 4000; 2000; 800 and 600), polyethylene glycol (M_w = 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 CO₂)

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

The total oils from the six condensers (C₁ to C₆) 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 (C₁ to C₆) 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 C₁₈ to C₃₀ with a maximum at C₂₄ (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 C₂₄ 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 α to the rings and 19.5% β 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 C₁₁ H₁₄ & C₁₁ H₁₆) 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 C₃ which falls down in C₅ and again reaches to the maximum at 18.5% in C₆. 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 α 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 α 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 ¹H-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. α and β 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	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 CH_2Cl_2 / Petroleum ether mixture, from 10 to 100% CH_2Cl_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	---	---	---	---	---	7.24 (1.3)
2	Furfural	0.28 (0.05)	0.37 (0.38)	0.44 (0.05)	0.89 (0.07)	0.52 (0.04)	0.50 (0.09)
3	Furfuryl alcohol	1.58 (0.28)	2.75 (0.37)	14.3 (1.5)	6.52 (0.51)*	4.64 (0.36)	2.45 (0.44)
4	Angellactone	0.68 (0.12)	2.90 (0.39)	0.48 (0.05)	---	---	---
5	Cyclohexanol	---	---	---	0.02 (0.002)	---	---
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)	---	2.75 (0.49)
12	Me-Cyclopentane-ol-one	0.14 (0.02)	0.82 (0.11)	1.81 (0.19)	4.35 (0.34)	1.54 (0.12)	---
13	m-Cresol	---	0.28 (0.35)	---	---	---	0.56 (0.1)
13a	p-Cresol	---	---	---	---	---	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)	---	---	0.64 (0.05)	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	Catrolone	1.13 (0.2)	2.01 (0.27)	2.48 (0.26)	4.6 (0.25)	7.73 (0.6)	5.02 (0.39)
22	Hydroquinone	---	---	---	---	0.52 (0.04)	8.35 (1.5)
23	Resorcinol	---	---	---	---	---	0.45 (0.08)
24	Syringol	1.81 (0.69)	2.37 (0.5)	10.86 (1.14)	10.23 (0.8)	5.02 (0.39)	12.48 (2.24)
25	Eugenol	3.11 (0.02)	0.45 (0.06)	0.28 (0.03)	0.26 (0.02)	0.26 (0.02)	---
27	Isosuganol	3.22 (0.57)	3.05 (0.41)	6.29 (0.66)	5.37 (0.42)	6.57 (0.51)	---
28	Vanilline	---	---	---	---	0.13 (0.01)	---
---	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.

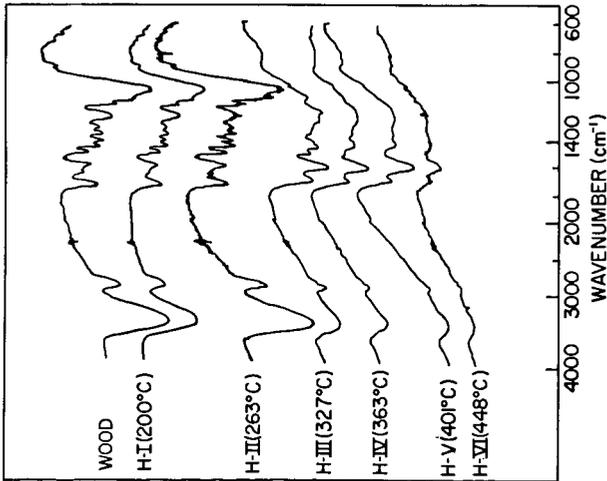


Fig. 1 - INFRARED SPECTRA OF WOOD AND SOLID RESIDUE. IN EACH SPECTRUM INDICATED BY H.,

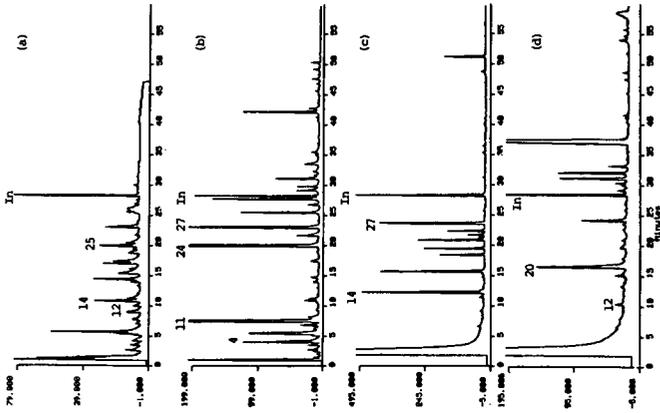


FIG. 2 - CAPILLARY GAS CHROMATOGRAMS OF: (a) total Condenser 6 oil; (b) Condenser 1 Fraction 1; (c) Condenser 2 Fraction 3 and (d) Condenser 3 Fraction 5. (See Table 2 for identification of peaks), In = Internal standard

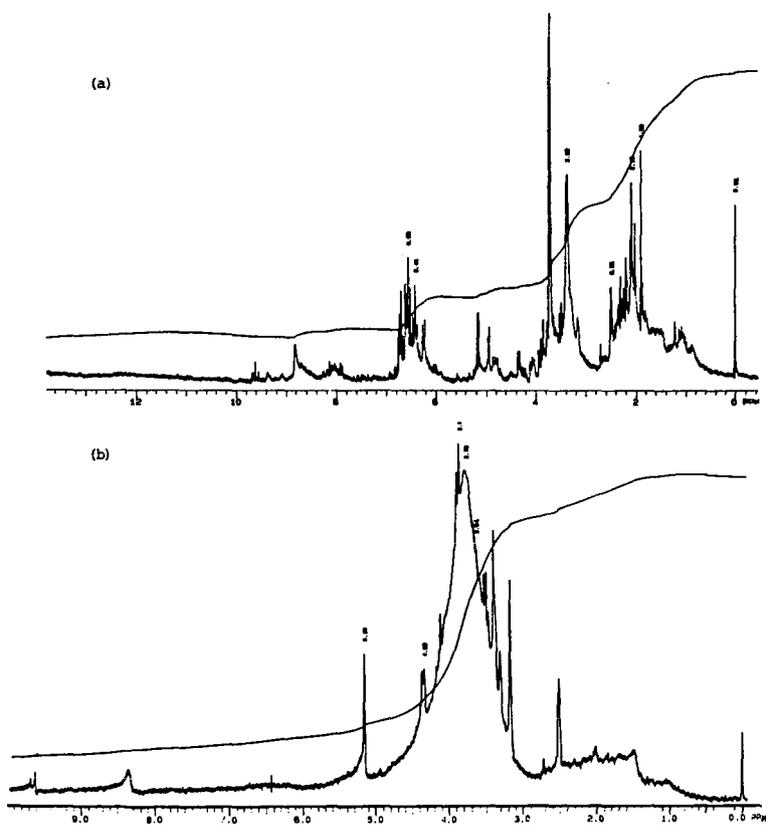


Fig. 3 - $^1\text{H-NMR}$ SPECTRA OF WOOD PYROLYTIC OILS
 (a) Condenser 6; (b) Fraction 13 Condenser 6

THE COMPOSITION OF OILS OBTAINED BY THE FAST PYROLYSIS OF DIFFERENT WOODS

J. Piskorz and D.S. Scott

Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

Introduction

During the last six years a fluidized bed fast pyrolysis process for biomass has been developed at the University of Waterloo (The Waterloo Fast Pyrolysis Process). This process gives yields of up to 70% of organic liquids from hardwoods or softwoods, which are the highest yet reported for a non-catalytic pyrolytic conversion process. A fluidized sand bed is used as a reactor and optimum liquid yields are normally obtained in the range of 450°-550°C at about 0.5 seconds gas residence time with particles of about 1.5 mm diameter or smaller. Two units are in use, one with a throughput of 20-100 gms/hr, and another with a throughput of 1-4 kg/hr. Details of the process have been published by the authors in several publications [1], [2], [3].

Several studies have been published describing results from the flash pyrolysis of biomass. Most of these studies were carried out at higher temperatures and were intended to promote biomass gas production. However, the work of Roy and Chornet [4] reported high liquid yields from biomass pyrolysis under vacuum conditions. More recently, Roy et al. [5] have described a vacuum pyrolysis system for the production of liquids from biomass, based on a multiple hearth type of reactor. Knight et al. [6] have developed an upward flow entrained pyrolyzer for the production of liquids from the thermal pyrolysis of biomass.

However, few details of the chemical nature of the pyrolytic oils produced from wood or other biomass have been reported. Some recent studies of the composition of pyrolysis oils obtained from poplar wood were carried out by workers of the Pacific Northwest Laboratories of Battelle Institute [7] and the Universite de Sherbrooke [8]. Methods of quantitative determination of functional groups in the pyrolytic oils from wood were tested in our laboratory by Nicolaides [9]. However, more detailed characterisation exists in the literature for the products of the thermal degradation of cellulose [10,11,12,13,14]

Results

In previously reported tests (3), yields have been classified as gases, organic liquids, char and product water. Mass balances generally close to 95% or better. Elemental analyses were also reported for many runs, but identification of individual compounds was done only for non-condensable gases and for some volatile organics such as methanol, acetaldehyde, furan,

etc. However, more detailed analyses of liquid products have recently been carried out, and some of these preliminary results which are of particular significance are reported here.

All experimental results given were obtained at conditions of close to optimal feed rate, particle size and residence time for maximum liquid yield at the stated temperatures, as determined by over 200 bench scale runs and 90 pilot scale runs.

Table 1 shows the experimental yields of products from selected runs for four different woods whose properties are given in Table 2.

High organic liquid yields are characteristic of all four materials when undergoing fast pyrolysis in our process. The total liquid yield, including water of reaction, varies from 70% to 80% of the dry biomass fed, all of which can be directly used as a substitute fuel oil if desired. The liquids are single-phase, homogeneous fluids, which pour readily, and which contain from 15% to 25% water depending on the feed material and its moisture content.

These liquids are quite stable at room temperature. The water content, in a period of twelve months, was found to increase slightly presumably due to the slow processes of condensation-polymerization going on even at room temperature. At higher temperatures, 120°C and above, the oils become increasingly unstable and decompose with evolution of gas, and finally charification of a polymeric residue. All the pyrolysis vapors produce an oil mist following rapid quenching, but their polar character allows the easy utilisation of electrostatic precipitation in the recovery system of a pyrolysis process.

Preliminary small scale combustion tests carried out with the pyrolysis oil as produced (20% water content) showed that it burns readily in a furnace with a conventional pressure atomizing burner, providing the combustion box is preheated. If an air atomizing nozzle is used with a pilot flame, no pre-heating of the combustion chamber is necessary. Larger scale tests for extended periods have not yet been done, but preliminary work shows that the pyrolysis oil has potential as a substitute fuel oil.

Some properties of "wet" liquids as produced are given in Table 3. The elemental analyses of the pyrolytic liquids as given in Table 3 are very similar to those of the starting materials - wood. One could probably fairly accurately describe these liquids, therefore, by the term "liquid wood". Two major characteristics of these liquids are high oxygen content and high density (much higher than wood). Another specific property is a limited water solubility. In the case of pyrolytic sirups produced by the Waterloo process, water is dissolved in the organic phase. The addition of more water to the level of about 60% by weight causes a phase separation and this behaviour has been utilized in our work for analytical purposes, in that both

fractions were analyzed separately after dilution of the original oil product.

The details of the HPLC technique developed for analysis of the water soluble fraction are given below:

Column : Aminex[®] HPX-87H, high performance
cation exchange resin in hydrogen form
300 x 7.8 mm from Biorad

Eluant : H₃PO₄ 0.007 N

Flow Rate : 0.80 ml/min, isocratic

Temperature : 65°C

Detector : Waters R 401 Differential Refractometer

Internal Standard : n-propanol

The quantitative data obtained by the HPLC technique are presented in Table 4. A typical HPLC-chromatogram is shown in Figure 1.

To obtain relative response factors and retention times, the pure compounds were fed and then eluted, although some of them, such as cellobiosan and 1,6 anhydro- β -D-glucofuranose, had to be synthesized in-house [13]. Confirmation of compound identification was obtained by GC-MS [Hewlett-Packard 5970 Mass Selective Detector coupled to 5890A Gas Chromatograph]. For GC-MS analysis, sugars and anhydrosugars were first trimethylsilylated to the corresponding ethers. Small amounts of simple phenols and of furanoid compounds were also detected by GC-MS in the water soluble fraction. These components were not quantified by HPLC.

The yields of the water insoluble fraction are given also in Table 4. This fraction separated as a dark brown viscous liquid which solidified during drying into a hard, black, easily powdered material.

The carbon-13 NMR spectrum of this pyrolytic product is shown in Figure 2 together with similar spectra published by Marchessault et al. [15] for milled wood lignin (MW) and steam exploded lignin (EXW). The similarity of the spectra of the steam exploded lignin and our pyrolytic lignin is quite striking. It appears that the oils produced by the Waterloo Fast Pyrolysis process contain a significant fraction which is apparently derived from the natural wood lignin. This "pyrolytic lignin" represents nearly 80% of the original content of wood lignin. Evidence for this conclusion was first reported from the work of H. Menard [16] using thermogravimetric and infrared analysis.

The Waterloo NMR spectrum was recorded using a 9% solution in DMSO-d₆ at 62.9 MHz and 50°C with broad-band proton decoupling. Delay time between pulses was 10 seconds.

Conclusions

Four different woods under conditions of fast pyrolysis yielded very similar liquid products. Analyses show that this product is a complex mixture of chemicals.

The pyrolytic "wet" tar-sirup can be readily separated into two principal fractions by water extraction. The water-insoluble fraction is derived from lignin while the water-soluble fraction is carbohydrate in origin. Analytical results indicate large amounts of low molecular weight (<100) lactones and aldehydes, and a significant fraction of these are multifunctional in nature. Four major classes of chemicals can be differentiated,

1. sugars and anhydrosugars
2. carbonyl and hydroxycarbonyl compounds
3. acids - formic, acetic
4. "pyrolytic" lignin.

Results in Table 4 show that 81-92% of the content of the pyrolysis oils produced in this work from wood has been quantitatively identified.

Detailed analysis of pyrolytic oils is needed in order to allow possible mechanistic or kinetic models to be formulated which can explain the various observed aspects of fast biomass thermal degradation. A knowledge of chemical composition of these oils may also assist in the eventual future utilization, up-grading or separation of these compounds as higher value products.

Acknowledgement

The financial support for this work of the National Research Council of Canada and of the Natural Sciences and Engineering Research Council of Canada are gratefully acknowledged by the authors. The assistance of P. Majerski and A. Grinshpun with experimental measurements is also acknowledged with pleasure.

References

- 1 D.S. Scott and J. Piskorz, Can. J. Chem. Eng., 60 (1982) 666
- 2 D.S. Scott and J. Piskorz, Can. J. Chem. Eng., 62 (1984) 404
- 3 D.S. Scott, J. Piskorz and D. Radlein, Ind. Eng. Chem. Process Res. Devel., 24 (1985) 581

- 4 C. Roy and E. Chornet, Proc. 2nd World Congress Chem. Eng., Montreal, Vol. II, 315, (1981)
- 5 C. Roy, A. Lalancette, B. DeCaumia, D. Blanchette, B. Cote, M. Renaud and P. Rivard, Bio Energy 84, H. Egnéus and A. Ellegard (Eds.) Vol. III, 31, (1984), Elsevier App. Sc. Publ., London
- 6 J.A. Knight, C.W. Gorton and D.J. Stevens, Bio Energy 84, H. Egnéus and A. Ellegard (Eds.) Vol. III, 9, (1984), Elsevier App. Sc. Publ., London
- 7 D.C. Elliott, International Energy Agency Co-operative Project D-1, Biomass Liquefaction Test Facility, National Energy Administration, Stockholm, Vol. 4
- 8 H. Ménard, D. Belanger, G. Chauvette, J. Khorami, M. Grise, A. Martel, E. Potvin, C. Roy and R. Langlois, in S. Hasnain (Editor), Proc. 5th Bioenergy R & D Seminar, Elsevier, New York, (1984), p.418
- 9 G.M. Nicolaidis, The Chemical Characterization of Pyrolysis Oils, MASC Thesis, Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, (1984)
- 10 F. Shafizadeh, J. Anal. Appl. Pyrol., 3 (1982), 283
- 11 T. Funazukuri, Ph.D. Thesis, Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, (1983)
- 12 J. Piskorz, D. Radlein, D.S. Scott, J. Anal. Appl. Pyr., 9 (1986) 121
- 13 D. Radlein, A. Grinshpun, J. Piskorz, D.S. Scott, J. Anal. Appl. Pyr., - accepted for publication (1986)
- 14 O.P. Golova, Russian Chemical Reviews, 44 (8), (1975)
- 15 R.H. Marchessault, S. Coulombe, H. Morikawa and D. Robert, Can. J. Chem., 60 (1982), 2372
- 16 H. Ménard, Université de Sherbrooke - private communication

Table 1
Pyrolysis Yields from Different Woods

	Brockville Poplar			White Spruce			Red Maple			IEA Poplar		
Kun #	51	58	50	42	43	45	14	63	81	27	59	A-2*
Temperature, °C	497	504	555	485	500	520	532	508	515	500	504	497
Moisture content, wt%	-	5.2	+	-	7.0	+	3.8	5.9	9.5	6.2	4.6	3.3
Particle Top Size, µm	-	1000	+	-	1000	+	590	590	1000	590	1000	590
Apparent Residence Time, sec	0.64	0.47	0.57	0.70	0.65	0.62	0.69	0.47	0.44	0.55	0.48	0.46
Feed Rate, kg/hr	2.24	2.10	4.12	2.07	1.91	1.58	2.16	1.98	1.32	2.24	1.85	0.05
Yields, wt% of m.f. wood												
Organic liquid	62.9	62.9	59.0	63.1	66.5	66.1	67.3	67.9	65.0	65.8	66.2	65.7
Water	10.3	9.7	10.2	10.7	11.6	11.1	7.4	9.8	10.0	9.3	10.7	12.2
Char	14.4	16.5	10.6	16.3	12.2	12.3	9.0	13.7	12.1	12.1	11.8	7.7
Gas:												
H ₂	0.02	0.02	0.07	0.04	0.02	0.01	0.04	0.01	0.02	0.02	0.01	--
CO	4.95	4.71	8.40	4.16	3.82	4.01	6.96	4.12	4.83	5.32	4.44	5.34
CO ₂	6.14	5.89	7.06	3.38	3.37	2.69	4.02	4.89	5.36	6.30	5.75	4.78
CH ₄	0.45	0.44	0.97	0.34	0.38	0.43	0.75	0.36	0.57	0.48	0.37	0.41
C ₂ H ₆	0.22	0.19	0.40	0.16	0.17	0.16	0.24	0.16	0.21	0.20	0.13	0.19
C ₂ H ₄	0.06	0.05	0.11	0.02	0.03	0.05		0.04	0.07	0.04	0.05	--
C ₁	0.06	0.07	0.10					0.07	0.10		0.08	0.09
C _n	0.13	0.16	0.28	0.03	0.04	0.06	0.04	0.14	0.41	0.09	0.19	3.10
Total Gas	12.0	11.5	17.4	8.1	7.8	7.4	12.1	9.8	11.6	12.4	11.0	10.8
Overall recovery wt%, m.f.	99.7	100.5	97.2	97.8	97.7	96.7	95.7	101.2	98.7	99.7	99.8	96.4

* Bench Scale Unit

Table 2
Properties of Feed Materials

Source	Whole Tree Poplar	White Spruce	Red Maple	IEA Poplar Wood
	Brockville Plantation, Whole Tree Except Leaves and Roots Ontario MNR Clone C-147	Eastern Canada Clean Wood Sawmill Sawdust and Mill Scrap		Clean Wood only Ontario MNR Clone D-38
Moisture, wt%	5.2	7.0	3.8 - 25.2	4.6
Ash, % of	1.19	0.50	0.40	0.46
Elemental Analysis, %				
C	49.06	49.63	48.5	49.45
H	6.23	6.36	6.1	6.05
O	43.6	43.1	--	44.4
N	1.08	0.2	--	0.07

Table 3
Properties of Pyrolytic Liquids

Run #	Brockville Poplar			White Spruce			Red Maple	IEA Poplar
	51	58	50	42	43	45	63	59
Yields, wt% of wood as fed	74.1	73.3	70.5	75.2	79.2	78.5	77.9	77.6
Water content, wt%	19.8	18.7	21.7	21.9	22.4	21.8	18.0	18.6
pH	2.6	2.4	2.8	2.1	2.1	2.3	2.4	2.4
Density, g/cc	1.19	1.20	1.18	1.22	1.22	1.22	1.19	1.23
Elemental analysis, wt%, m.f.								
Carbon	54.1	54.7	55.6	53.5	54.0	56.6	54.7	53.6
Hydrogen	7.1	6.9	6.9	6.6	6.8	6.9	6.4	7.0

Table 4
Analysis of Liquid Products

Run #	Brockville Poplar	White Spruce	Red Maple	IEA Poplar
Temperature	504	500	508	A-2 504
Yields, wt% of feed, m.f.				
organic liquid	62.9	61.5	67.9	69.8
1. oligosaccharides				0.70
2. cellobiosan	1.11	2.49	1.62	1.30
3. glucose	0.55	0.99	0.64	0.41
4. fructose	1.34	2.27	1.51	1.32
5. glyoxal	1.42	2.47	1.75	2.18
6. methylglyoxal				0.65
7. levoglucosan	2.52	3.96	2.84	3.04
8. 1,6 anhydroglucofuranose	--	--	--	2.43
9. hydroxyacetaldehyde	6.47	7.67	7.55	10.03
10. formic acid	5.40	7.15	6.35	3.09
11. formaldehyde	--	--	--	1.16
12. acetic acid	6.30	3.86	5.81	5.43
13. ethylene glycol	0.87	0.89	0.63	1.05
14. acetol	1.70	1.24	1.15	1.40
15. acetaldehyde	--	--	--	0.02
16. methanol				
Water-solubles-total above	27.7	33.0	29.9	34.2
Pyrolytic lignin	24.8	20.6	20.9	16.2
Amount not accounted for (losses, water soluble phenols, furans etc.)	10.5	7.9	17.1	18.3

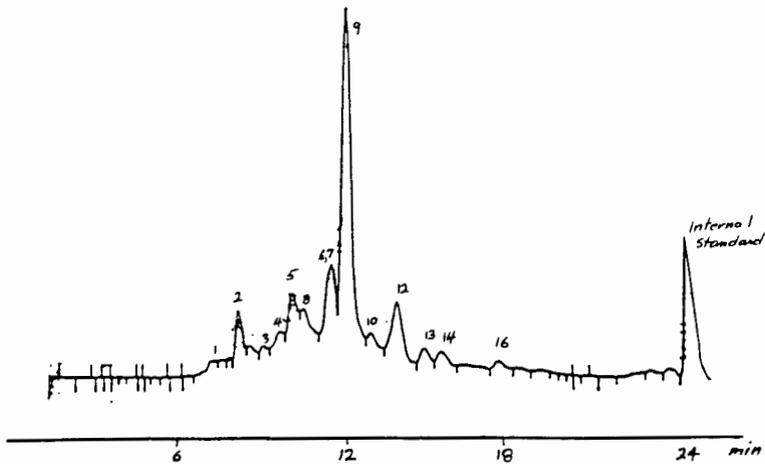


Figure 1 Chromatogram of Wood tar from run # A-2

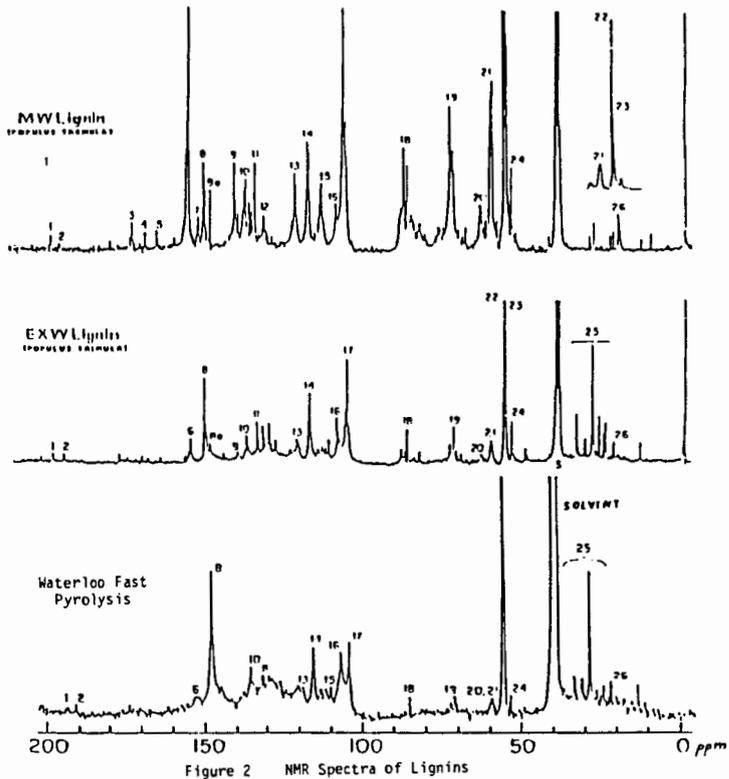


Figure 2 NMR Spectra of Lignins