

**Some Aspects of Pyrolysis Oils Characterization
by High Performance Size Exclusion Chromatography (HPSEC)**

David K. Johnson and Helena Li Chum*,

Chemical Conversion Research Branch
Solar Energy Research Institute
1617 Cole Blvd., Golden, Colorado 80401

ABSTRACT

The utilization of biomass pyrolysis oils or isolated fractions of these feedstocks requires a fast overall characterization technique. Gas chromatographic techniques typically analyze only the volatile fraction (5%-50%) of underivatized oils. With proper choice of solvent and detector systems, the HPSEC on polystyrene-divinylbenzene copolymer gels of the whole oils can provide valuable information on the apparent molecular weight distributions and changes that occur upon aging or chemical fractionation. Several pyrolysis oils have been analyzed as well as fractions isolated by solvent elution chromatography. In order to understand better the observed low-molecular-weight region, a number of model substances of the main classes of compounds found in pyrolysis oils have been investigated. While hydrogen bonding between the phenolic groups and tetrahydrofuran occurs, solute-solute interactions can be kept very small by operating at very low concentrations of solute; solute-gel interactions do occur when polycyclic aromatic compounds predominate. HPSEC provides very good information on shelf life, reactivity of pyrolysis oils, and comparison of oils as a function of process conditions.

INTRODUCTION

Many biomass pyrolysis processes produce 55%-65% conversion of the dry biomass to a very inexpensive pyrolysis oil (1-3). Costs of the oils will range from \$0.02-\$0.08/lb of oil, depending on the biomass feedstock cost (\$10-\$40/dry ton biomass). Therefore, these inexpensive oils, rich in phenolic fractions, acids, and furan-derivatives can be feedstocks for further upgrading or could be used because of their reactivity, in applications such as thermosetting resins and other wood-bonding methods. One of the important considerations for this use or further processing is the stability of the oil. Fast techniques to determine such properties become necessary. We present a method of characterization of pyrolysis oils and chemically isolated fractions using high-performance size exclusion chromatography (4-5), a technique commonly employed in the determination of the molecular weight distribution of polymers. We discuss the potential of the method and its limitations. Classes of model compounds commonly found in these oils have been investigated in the low-molecular-weight range to shed light on interactions between solute and solvent, solute and gel material (polystyrene-divinylbenzene), and solute-solute which can be kept to a minimum by operating at very dilute conditions.

EXPERIMENTAL

High performance size exclusion chromatography was performed on Hewlett-Packard 1084 and 1090 liquid chromatographs using HP1040A diode array and HP-1037A refractive index detectors. Data were stored on a HP 85 microcomputer. The columns (300 x 7 mm) used in this study were purchased from Polymer Laboratories Inc. and were a PL 100 A (10 μ particles) and a PL 50 A (5 μ particles). The solvent employed was tetrahydrofuran (Burdick and Jackson, chromatographic grade) used as received.

Details on the preparation of pyrolysis oils at SERI in the entrained-flow, fast ablative pyrolysis reactor can be found in a report by Diebold and Scahill (2).

The lignin model compounds were prepared by J. A. Hyatt (6); all the other model compounds were purchased from the Aldrich Chemical Co.

RESULTS AND DISCUSSION

Comparison of Pyrolysis Oils Obtained from Various Sources. The HPSEC of four wood pyrolysis oils obtained from the entrained flow, fast ablative pyrolysis reactor at SERI are shown in Figure 1. The oils were obtained from two separate runs and collected from two different scrubbers. The apparent molecular weight distributions of the four oils are very similar, indicating little selectivity on the basis of molecular weight distribution. Figure 2, however, shows the HPSEC chromatograms of a number of other pyrolysis oils obtained under a variety of conditions from many different sources. Clearly, some of the oils contain components of high apparent molecular weight even to the extent that some are excluded from the pores of the column polymer, indicated by the peaks at about 4.5 minutes in the chromatograms. The oils also have varying amounts of more sharply resolved components at lower apparent molecular weight. Thus, HPSEC may be used to characterize pyrolysis oils obtained from different sources, and comparisons may be drawn regarding their relative apparent molecular weight distributions as long as the analyses were carried out under the same chromatographic conditions.

The wood oil obtained from the packed scrubber in Run 41 at SERI was also subjected to fractionation by sequential elution by solvents chromatography (SESC) according to the method of Davis et al. (7). The fractions obtained were also analyzed by HPSEC and the chromatograms are shown in Figure 3. The HPSEC shows a general trend to higher apparent molecular weight as the polarity of the eluting solvent was increased up to methanol. A number of the fractions appear to contain relatively large amounts of distinct components (the sharp peaks) of lower apparent molecular weight. The sixth fraction was produced by going back to a less polar solvent. A seventh fraction was produced using a more polar eluant of 10% acetic acid in methanol which could not be analyzed by HPSEC because it was insoluble in tetrahydrofuran. About three-quarters of the oil was found in Fractions 3, 4, and 5, the last being the major fraction. If the chromatograms in Figure 3 were combined taking into account the yields of the various fractions then, as expected, a close comparison could be made with the chromatogram in Figure 1 of the unfractionated oil.

Doubts have been expressed that these pyrolysis oils could have molecular weights as high as indicated by these chromatograms as they are obtained by condensation of the primary vapors from pyrolysis. Analysis by techniques requiring revaporization of the oils consistently does not detect high-molecular-weight components, possibly because they are difficult to vaporize and also because they may be thermally degraded to either higher or lower molecular weight components (8) or both. It has been suggested that the high apparent molecular weights observed by HPSEC are the result of solute-solute or solute-solvent associations producing high-molecular-weight complexes. To verify the results obtained by HPSEC, the three major fractions and the original unfractionated oil were subjected to proton NMR analysis. The spectra of Fraction 5 and the original oil contain broad peaks characteristic of irregular polymers such as lignin, while the spectrum of Fraction 3 contains sharp peaks indicative of a mixture of simpler, low-molecular-weight compounds; Fraction 4 is intermediate between 3 and 5. Thus, the HPSEC and proton NMR spectra appear to be in general agreement in that this pyrolysis oil

contains mixtures of possibly higher molecular weight polymeric components and simpler low-molecular-weight compounds.

Many of the chromatograms shown here are of samples whose history of handling and age are not known in detail. It has been suggested that because of the very reactive and acidic nature of these oils that the high molecular weights observed are produced as the oils get older and are exposed to ambient conditions. Consequently, a study has been started to examine the effects of aging and the conditions under which pyrolysis oils are stored. A pyrolysis oil was produced in the SERI entrained-flow, fast ablative pyrolysis reactor. In this reactor, the primary vapors are scrubbed out with water such that about 90% are dissolved out. One sample of this aqueous solution of pyrolysis oil was stored at 4°C and the other was analyzed by HPSEC. The sample to be analyzed was made up by dissolving a small amount of the aqueous solution in tetrahydrofuran. Storage was under ambient conditions. The THF solution was analyzed several times over the period of a week to look for changes in its HPSEC chromatogram as shown in Figure 4. At the end of this period, the sample kept at 4°C was also analyzed to determine the effect of aging on the oil. Actually, a physical change took place on the aqueous sample stored at 4°C in that a small amount of tar separated out on the bottom of the vial. Consequently, two samples were made up in THF from the cooled sample, one from the aqueous part and one from the tar. Figure 5 compares the HPSEC of the sample kept at ambient conditions to those of the cooled samples. The HPSEC of the tar sample shows it consists of relatively much larger amounts of material higher in apparent molecular weight. The aqueous fraction of the cooled sample appears very similar to the sample stored at 25°C, although the latter does appear to contain a slightly larger relative amount of apparently higher molecular weight material. The degree to which storage at lower temperature has prevented any increase in molecular weight of the pyrolysis oil with time is difficult to ascertain because of the fractionation of the refrigerated sample. The sample kept at ambient conditions did not have the opportunity to fractionate because of the solvent it was dissolved in.

The HPSEC of the unrefrigerated sample (Figure 4) did indicate that the pyrolysis oil "aged" over the period of a week with increasing amounts of apparently higher molecular weight components being produced with time. Most of the samples obtained from outside of SERI are much older than one week. Pyrolysis oils are generally very reactive so that unless they are effectively stabilized in some way, increasing molecular weight should be expected as they get older.

What are the Limitations of HPSEC as a Technique When Applied to Pyrolysis Oil Characterization. One of the major advantages of HPSEC as a technique is that with the proper choice of solvent to dissolve the sample, the whole of the sample may be analyzed under very mild conditions. Because HPSEC is an isocratic technique, differential refractometers may be used as detectors so that, again, all of the sample may be detected. This is not a great concern when applied to pyrolysis oils, as they tend to absorb quite strongly in the ultraviolet. With a modern UV-visible diode array detector, a number of wavelengths can be monitored to ensure all the components of the oil are monitored. However, the eluting solvent must be chosen such that all the sample is dissolved, and as pyrolysis oils are fairly polar and often contain water, the solvent will also need to be fairly polar. The combination of polar solutes and polar solvents means that solute-solvent interactions through hydrogen bonding must be a concern. Tetrahydrofuran, probably the most popular solvent for HPSEC, can form hydrogen bonds with certain species such as phenols producing a complex molecule exhibiting greater molecular size and lower retention volume than would be expected (9). When nonpolar solvents are used such as toluene or chloroform, the molecular size should be relatively unaffected, but oil solubility then becomes very limited. The use of solvents of greater solvating

power, such as dimethyl formamide, also generates problems (10) due to solute-solute association, interaction between polystyrene standards and the column gel and column gel-solvent interactions.

The other major limitation of HPSEC as a technique comes from the desire to correlate solute elution time with molecular weight. As stated in its name, this is a method of separation based on molecular size. HPSEC columns contain a polymer gel of polystyrene-divinylbenzene produced with a controlled pore size distribution. Solutes of different size are separated by the different degrees of their penetration into the pores of the gel. The parameter that can be obtained from HPSEC is effective molecular length; e.g., material excluded from a column containing gel with 100 Å pores should have an effective molecular length of 100 Å or greater. To correlate retention times to molecular weight, it is necessary to use calibration standards similar in structure to the solute whose molecular weight is being determined. The most common calibration materials used are polystyrenes of low polydispersity. Others used include straight chain alkanes, polyethylene glycols, and the related materials IGEALS™ that are 4-nonylphenyl terminated. If a column were calibrated with straight chain alkanes, it is unlikely to be much good for obtaining molecular weights of aromatic solutes, as a benzene ring is only about as long as propane, and anthracene is only about as long as hexane. When dealing with much larger molecules, it is difficult to estimate what their size might be in three dimensions in solution. Although pyrolysis oils have a high level of aromatic components, especially phenolics, they are a very complex mixture of components, and so it is unlikely that any one set of calibration standards would do a very good job. Despite these limitations, HPSEC can give an idea of the molecular weight distribution of an oil and certainly can be used in comparing oils. Establishing molecular weights for low-molecular-weight components is probably the most difficult task. Figures 6 and 7 compare the actual molecular weights of a variety of different types of compounds with their apparent molecular weights calculated from their retention times on 50 Å 5 μ HPSEC column calibrated with polystyrenes and IGEALS. If the calibration was good for all compounds, then they should all fall on the straight lines. The aromatic hydrocarbons follow the calibration, but the aromatic acids and naphthalenes deviate greatly and in opposite directions. The aromatic acids contain both carboxylic and phenolic groups and so probably have higher apparent molecular weights than their actual molecular weights because of hydrogen bonding with the solvent tetrahydrofuran. The naphthalenes have lower apparent molecular weights than actual not only because their condensed structure makes them relatively small for their molecular weight, but also because of interactions between these solutes and the column gel. Philip and Anthony (9) observed retention volumes that were longer than expected for anthracene, benzopyrene, and coronene, considering their molecular size. They attributed this behavior to interaction of these highly aromatic solutes with the phenyl groups of the polymer chains of the gels.

The phenols and lignin model compounds follow the calibration quite closely, tending to show slightly higher apparent molecular weights than they actually have, probably because of association with the solvent. This is encouraging for the HPSEC of pyrolysis oils as these types of compounds are more likely to be present. Heavily cracked oils, however, can be rich in polynuclear aromatics.

Solute-solute association has not been observed for any of these molecules or for others when using tetrahydrofuran as solvent. Retention time changes of less than 0.01 minutes were observed in changing sample concentrations in the mg/mL range (~4 mg/mL) to the ng/mL range (~3 μg/mL) when injecting 5 μl of these solutions. HPSEC of pyrolysis oil samples made up in this concentration range should also be free of

solute-solute association which would artificially increase the apparent molecular weight of the oils.

CONCLUSIONS

HPSEC has been shown to be a useful method of characterizing pyrolysis oils because it examines the whole of the oil. Using polystyrene-divinyl benzene polymer gel columns, tetrahydrofuran as solvent and polystyrenes and IGEALS as calibration standards a good indication of molecular weight distribution can be obtained for oils from a variety of sources. The high apparent molecular weights observed appear to be real, and some corroboration is seen in proton NMR spectra. Although some solute-solvent association can be expected, use of phenolic model compounds has shown that HPSEC can give a good indication of molecular weight. However, if the oils contained large amounts of either much more polar compounds or condensed aromatic compounds, then interpretation of HPSEC on the basis of molecular weight would be much more difficult. Pyrolysis oils are reactive materials and an awareness of the length of time and conditions under which they are kept must be maintained and is important for further processing.

ACKNOWLEDGEMENTS

This work was supported by the Office of Industrial Programs of the U.S. Department of Energy (FTP 587). Thanks are due to Mr. A. Schroeder, Program Manager, and to all producers of pyrolysis oils: J. Diebold, Tom Reed, J. Scahill, C. Roy, S. Kaliaguine, J. Howard, and to R. Evans and T. Milne for profitable discussions. Thanks also to J. A. Hyatt for supplying three of the lignin model compounds employed.

REFERENCES

- (1) Diebold, J. P., Editor, Proc. Specialists Workshop on Fast Pyrolysis of Biomass, Copper Mountain, October 1980, SERI/CP-622-1096, Golden, Colorado: Solar Energy Research Institute.
- (2) Diebold, J. P., and Scahill, J. W., "Entrained-Flow Fast Ablative Pyrolysis of Biomass," SERI/PR-234-2665, 1985, Golden, Colorado: Solar Energy Research Institute.
- (3) Overend, R. P., and Milne, T. A.; and Mudge, L. K., Editors, Fundamentals of Thermochemical Biomass Conversion, Elsevier: NY, 1985.
- (4) Provder, T., Editor, Size Exclusion Chromatography: Methodology and Characterization of Polymers and Related Materials, ACS Symposium Series, 245, Washington, D.C., ACS (1984).
- (5) Yau, W. W.; Kirland, J. J.; and Bly, D. D., Modern Size Exclusion Chromatography: Practice of Gel Permeation and Gel Filtration Chromatography Wiley: New York (1979).
- (6) Hyatt, J. A., Synthesis of Some Tetrameric Lignin Model Compounds Containing β -0-4 and 5,5'-Interunit Linkages, to appear in Holzforschung.
- (7) Davis, H. G.; Eames, M. A.; Figueroa, C.; Gansley, K. K.; Schaleger, L. L.; and Watt, D. W., 1985, "The Products of Direct Liquefaction of Biomass," Fundamentals of Thermochemical Biomass Conversion, edited by R. P. Coverend, T. A. Milne, and L. K. Mudge, London: Elsevier Applied Science Publishers, pp. 1027-1038.

(8) Evans, R. J., and Milne, T. A., Molecular Characterization of the Pyrolysis of Biomass. II. Applications, submitted to Energy and Fuels.

(9) Philip, C. V., and Anthony, R. G., "Analysis of Petroleum Crude and Distillates by Gel Permeation Chromatography," ACS Symposium Series 245 (17), 257-270 (1984).

(10) Chum, H. L.; Johnson, D. K.; Tucker, M.; Himmel, M., Performance Size Exclusion Chromatography using Styrene-Divinylbenzene Copolymer Gels, Holzforchung in press.

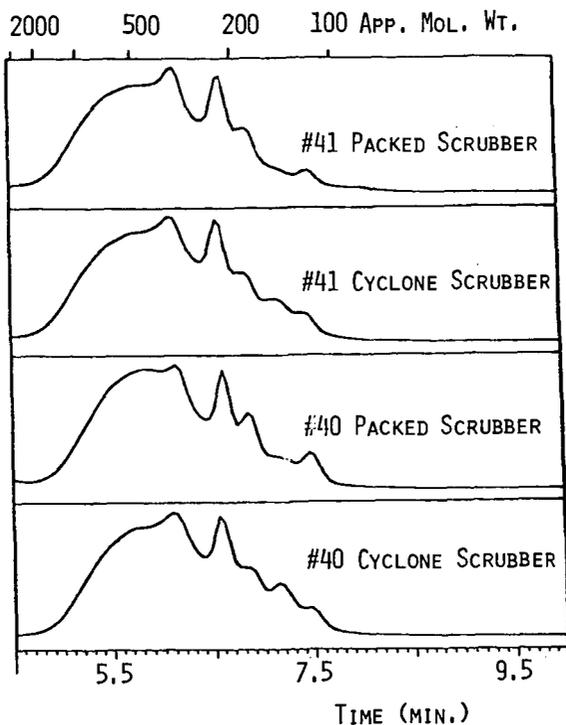


FIGURE 1. HPSEC OF WOOD PYROLYSIS OILS FROM THE SERI ENTRAINED-FLOW, FAST ABLATIVE PYROLYSIS REACTOR. ANALYSIS ON PL GEL 100Å, 10 μ GPC COLUMN USING THF AT 1 mL MIN⁻¹ WITH DETECTION AT 330 NM (BANDWIDTH 140 NM).

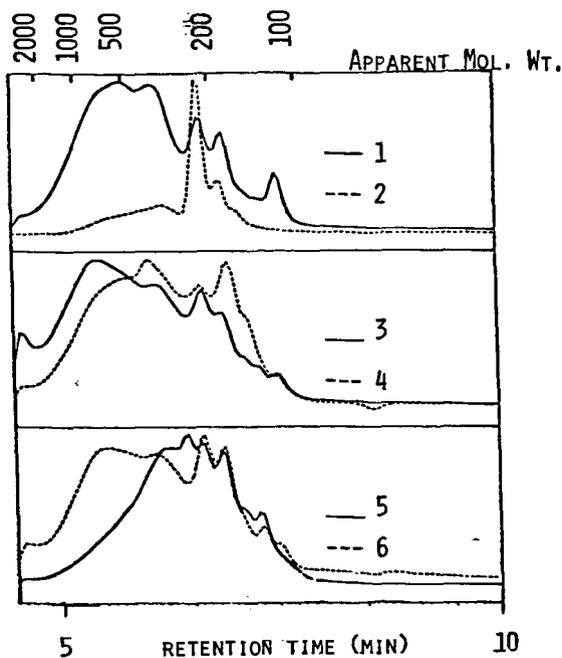


FIGURE 2. HPSEC OF WOOD PYROLYSIS OILS FROM A VARIETY OF SOURCES. ANALYSIS CONDITIONS AS PER FIGURE 1.

- 1 = OIL FROM D. S. SCOTT, U. OF WATERLOO, FLASH PYROLYSIS OF HYBRID POPLAR-ASPEN.
- 2 = OIL FROM C. ROY, U. DE SHERBROOKE, VACUUM PYROLYSIS OF AVICEL @ 306°C.
- 3 = OIL FROM C. ROY, U. DE SHERBROOKE, VACUUM PYROLYSIS OF ASPEN POPLAR @ 534°C, 2.2 MM OF HG.
- 4 = OIL FROM J. HOWARD, B. C. RESEARCH, SUPERCRITICAL ACETONE EXTRACTION OF ASPEN.
- 5 = OIL FROM S. KALIAQUINE, U. OF LAVAL, SUPERCRITICAL METHANOL EXTRACTION OF ASPEN @ 350°C, 1500 PSI.
- 6 = OIL FROM C. ROY, U. DE SHERBROOKE, VACUUM PYROLYSIS OF ASPEN @ 315°C, 0.7 MM OF HG.

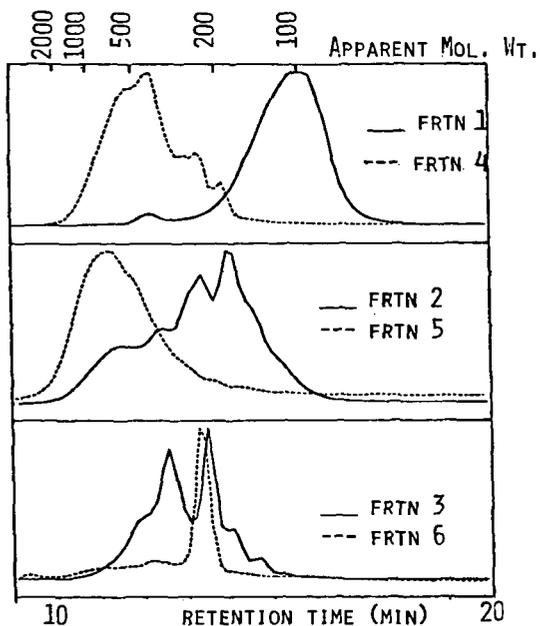


FIGURE 3. HPSEC OF SESC FRACTIONS FROM WOOD PYROLYSIS OIL RUN #41 PACKED SCRUBBER. ANALYSIS ON PL GEL 100 Å 10 μ GPC COLUMN USING THF AT 0.5 ML MIN⁻¹ WITH DETECTION AT 330 NM (BANDWIDTH 140 NM).

FRACTION 1 ELUTED WITH 15% TOLUENE IN HEXANE, YIELD 0.4%.

FRACTION 2 ELUTED WITH CHLOROFORM, YIELD 1.5%.

FRACTION 3 ELUTED WITH 7.5% ETHER IN CHLOROFORM, YIELD 15.6%.

FRACTION 4 ELUTED WITH 5% ETHANOL IN ETHER, YIELD 19.5%.

FRACTION 5 ELUTED WITH METHANOL, YIELD 38.1%.

FRACTION 6 ELUTED WITH 4% ETHANOL IN THF, YIELD 3.1%.

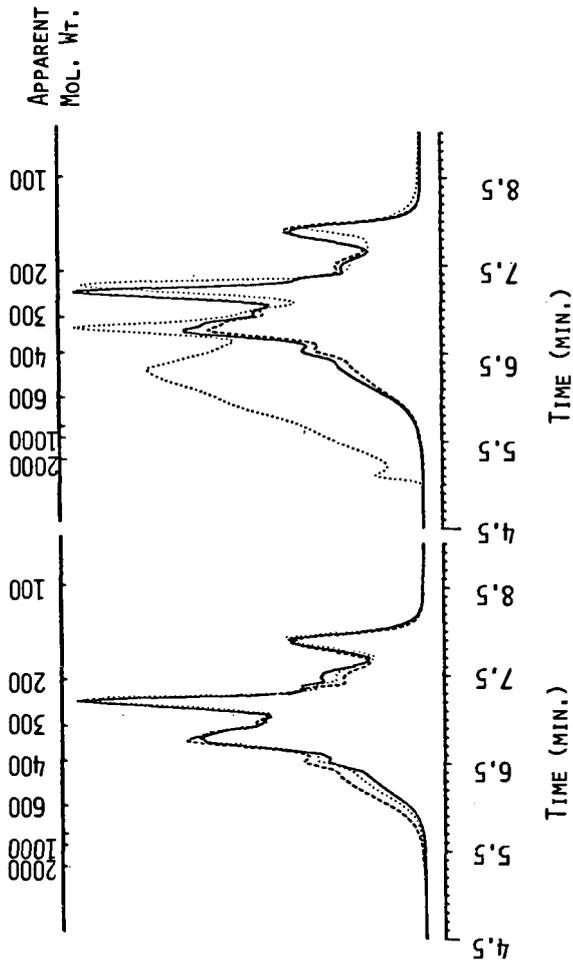


FIGURE 4. HPSEC OF PYROLYSIS OIL KEPT UNDER AMBIENT CONDITIONS AFTER 5 HRS (—), 3 DAYS (...), AND 7 DAYS (---). ANALYZED ON A PL GEL 50 Å, 5 μ GPC COLUMN USING THF AT 1 ML MIN⁻¹ WITH DETECTION AT 270 NM (BANDWIDTH 10 NM).

FIGURE 5. HPSEC OF PYROLYSIS OIL AFTER 7 DAYS KEPT UNDER AMBIENT CONDITIONS (—), TAR FRACTION OF REFRIGERATED SAMPLE (...) AND AQUEOUS FRACTION OF REFRIGERATED SAMPLE (---). ANALYSIS CONDITIONS AS PER FIGURE 4.

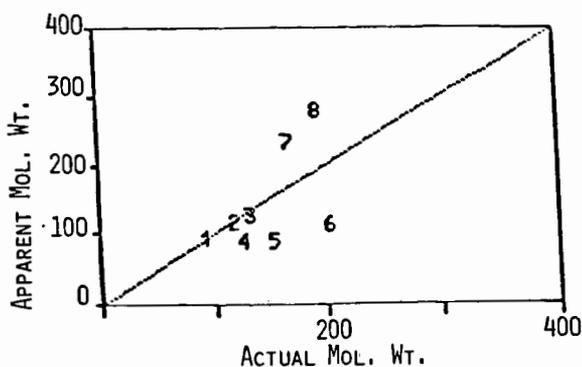


FIGURE 6. APPLICABILITY OF CALIBRATION FOR AROMATIC HYDROCARBONS, ACIDS, AND NAPHTHALENES. 1 = TOLUENE; 2 = PROPYL BENZENE; 3 = S-BUTYL BENZENE; 4 = NAPHTHALENE; 5 = 1,4-DIMETHYL NAPHTHALENE; 6 = 1-PHENYL NAPHTHALENE; 7 = VANILLIC ACID; 8 = 4-HYDROXY-3-METHOXY CINNAMIC ACID.

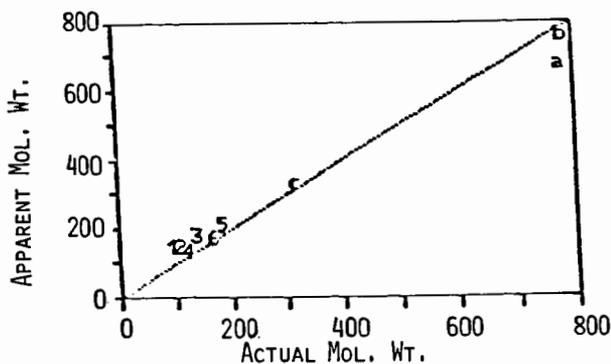


FIGURE 7. APPLICABILITY OF CALIBRATION FOR PHENOLS AND LIGNIN MODEL COMPOUNDS.

1 = PHENOL; 2 = P-CRESOL; 3 = 2-PROPYL PHENOL; 4 = GUAIACOL; 5 = SYRINGYL ALCOHOL; 6 = ACETOVANILLONE. LIGNIN MODELS: SEE

REF. 6 FOR DETAILED DESCRIPTION.

A = 5,5'-BIPHENYL TETRAMER HEXAOL, $C_{42}H_{54}O_{14}$

B = β -O-4 TETRAMER HEPTAOL, $C_{41}H_{52}O_{15}$

C = β -O-4 DIMER TRIOL, $C_{17}H_{20}O_6$.