

## Molecular-Beam, Mass-Spectrometric Studies of Wood Vapor and Model Compounds over HZSM-5 Catalyst

Robert J. Evans and Thomas A. Milne

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

### INTRODUCTION

Following research and development successes in the gasification of biomass (1), the biomass component of DOE's Biofuels and Municipal Waste Technology Division program is emphasizing direct liquefaction processes to premium hydrocarbon fuels (2). The approach being explored at SERI involves an integrated, ambient-pressure process in which primary wood pyrolysis vapor is formed by fast pyrolysis and immediately passed over a shape-selective catalyst to remove oxygen as H<sub>2</sub>O, CO, and CO<sub>2</sub>. A leading vapor production method and the engineering aspects of this process are discussed by Diebold in two companion papers in this symposium (3, 4).

We report here preliminary screening results on the behavior of wood pyrolysis vapor and model compounds when passed, at high dilution, over a sample of HZSM-5 supplied by the Mobil Corporation (5).

### EXPERIMENTAL

The screening is carried out using a simple, quartz, two-stage reactor coupled to a free-jet, molecular-beam, mass-spectrometer sampling system. This system and typical results for primary and secondary vapors from wood and its constituents are described in a recent publication (6). Carrier gas (He for the results shown below) is preheated in a 30 cm lower section of 2 cm ID quartz. A side arm allows introduction of solid samples to the hot gas or injection of liquids or gases through syringes. The upper 30 cm long section contains the catalyst, placed at the center of the upper section for temperature uniformity.

The catalysts used in this work are: (1) medium pore sized H-ZSM5 provided by Mobil (MCSG-2, extrudate with an unspecified amount of alumina binder); (2) medium pore sized Silicalite provided by Union Carbide (S-115, extrudate with 20% alumina); (3) large pore sized type Y Molecular Sieve provided by Union Carbide (SK-500, extrudate) and (4) silica/alumina obtained from Davidson (980-13, extrudate).

Gases and vapors emerging from the quartz reactor are immediately extracted by a sonic orifice and converted by a second orifice to a molecular beam. Expansion to molecular flow ensures rapid quenching and presents a sample to the ion source of the mass spectrometer that has not suffered wall collisions. In this way, highly condensible species can be sampled in real time. The data shown below are positive ion mass spectra using low energy (22.5 eV) electrons to minimize fragmentation.

This system has the advantage of allowing observation of the actual vapor species that enter the catalyst space and the easy observation of the breakthrough of reactant species. All product species but H<sub>2</sub> can be followed, but fragmentation occasionally interferes and isomers cannot be separately detected. At the moment, the technique is semi-quantitative and is viewed as a supplement to bench-scale systems with product collection for GC analysis, mass balances, and coke determinations (4).

## RESULTS AND DISCUSSION

The goals of this catalyst screening project are to gain insight into the conversion of biomass pyrolysis products with a variety of catalysts and under a range of conditions. The screening results allow an assessment of several important aspects of the conversion process: the identification of promising catalysts; the determination of the critical variables in yield optimization; the effect of catalyst composition, structural properties, and physical form on product formation; the behavior of model compounds that represent the range of functionality and structure found in biomass pyrolysis vapors; the determination of relative coking rates for various catalysts and feedstocks; and the regenerability of catalysts. This experimental system was designed to study biomass pyrolysis vapors and has been used to study the fundamentals of biomass pyrolysis, both the initial condensed phase pyrolysis and the subsequent vapor phase pyrolysis (6).

This screening approach is not a stand-alone technique, however, and hence scale experimentation is needed to provide data for parameters which the screening approach does not adequately address: confirmed product identification, product mass balance, long-term studies in assessing catalyst life, and the variation of certain reactor operating conditions which have limited ranges at this scale, such as feed partial pressure or carrier gas flow rate. Initial results are reported here for the effect of the type of catalyst, the effect of weight hourly space velocity (WHSV) and temperature, the estimation of product yields, and the effect of cofeeding methanol for wood vapor conversion to organic products. The relative performance of several model compounds over H-ZSM5 has also been examined and preliminary results are presented.

The relative activities and behavior of four catalysts are shown in Figure 1 which compares the mass spectra of the products. The low-molecular-weight products ( $m/z$ 's 18-44) are under-represented in the spectra due to discrimination of the detection system against low masses in these particular experiments. Nevertheless, the uncorrected spectra are sufficient for comparing different catalysts. The H-ZSM5 zeolite was the catalyst used for most of the work in this paper. The Silicalite is also a shape selective catalyst with the ZSM-5 structure, but with nearly zero aluminum in the crystal lattice. The Silicalite gave the same type of products as H-ZSM5, but with differences in the proportions. The formation of light aromatics [benzene ( $m/z$  78), toluene ( $m/z$  92), xylene ( $m/z$  106)], furans [furan ( $m/z$  68) and methyl furan ( $m/z$  82)], alkenes [propylene ( $m/z$  42) and butene ( $m/z$  56)], and naphthalenes [naphthalene ( $m/z$  128) and methyl-naphthalene ( $m/z$  142)] are the major classes of products from wood pyrolysis product conversion over zeolite catalysts. The furans are intermediates that can be subsequently converted to other products with higher reaction severity (i.e., lower WHSV or higher temperatures). The naphthalenes are formed under higher reaction severity and are most likely undesirable products for most applications. The shape-selective nature of these two catalysts is apparent. There is no selectivity observed in the destruction of the wood pyrolysis vapors, as all pyrolysis products are destroyed. However, the higher molecular weight primary products may be converted to coke on the macrosurface of the catalyst, as will be discussed below. The Silicalite appears to be less reactive than the H-ZSM5 since fewer aromatics are formed relative to  $CO_2$  ( $m/z$  44) for the Silicalite, more furan is formed relative to the aromatics, more high-molecular-weight material survives (that is probably associated with the wood primary pyrolysis products), and less of the heavier alkylnaphthalenes are formed relative to the light aromatics.

The third catalyst shown in Figure 1 is a crystalline aluminosilicate derived from a wide bore, type Y molecular sieve that shows significantly less activity than the

H-ZSM5 and silicalite. The intermediate furans are comparable to the light aromatics and unreacted wood pyrolysis products ( $m/z$ 's 60, 98, 124, 150 and 164) are present in the spectrum. Olefin yields appear higher than for the first two catalysts, however.

The fourth catalyst in Figure 1 is a silica/alumina catalyst which also shows the intermediate conversion slate (i.e., furans and unreacted pyrolysis products), indicating low activity. The peaks at  $m/z$ 's 134, 148, and 162 have higher relative abundance than in the spectra from the other three catalysts and are likely due to tetra-, penta-, and hexamethylbenzene which form in higher amounts than toluene, xylene, and trimethylbenzene because of the lack of shape selectivity, which limits the product size with the zeolite catalysts.

The proportions of organic products that form from wood vapor over H-ZSM5 vary systematically with WHSV and temperature. The effects of these two parameters on the relative abundance of selected products from the conversion of pine pyrolysis products over H-ZSM5 are shown in Figure 2. The temperature was varied from 300° to 550°C and the WHSV from 0.7 to 2.0 hr<sup>-1</sup>. These are compositional plots and do not directly show the yield of these components since coke will vary with these parameters and is not reflected in the product distribution. The plots of trimethylbenzene, toluene, and benzene show a trend for dealkylation with increased temperature. Trimethylbenzene decreases with temperature, while toluene increases to a maximum at 500°C and then decreases at higher temperatures. A possible explanation is that the dealkylation of trimethylbenzene and xylene lead to increased abundances of toluene, reaching a maximum at 500°C where the depletion of these heavier species and the dealkylation of toluene leads to a decrease in its relative abundance. Benzene increased throughout the temperature range studied. At higher temperatures, benzene relative abundance also increased with lower WHSV's.

The few intermediates from wood vapor are represented in Figure 2 by  $m/z$  118 (probably benzofuran), which shows a maxima at 400°C for all three WHSV's, although the relative abundance increases with WHSV. The alkenes show a steady increase with temperature and a dependence on WHSV at the higher temperatures. The generation of alkenes under extreme reaction conditions possibly indicates that the mechanism of aromatic formation from the alkenes in methanol conversion is not followed in wood pyrolysis product conversion. The aromatics formed from wood are possibly formed more directly by the dehydration and aromatization of the primary pyrolysis products rather than from the polymerization of alkenes as in methanol conversion. The formation of condensed aromatics is also enhanced at higher temperatures, as demonstrated by naphthalene in Figure 2. The trend of lower yields of naphthalenes with lower WHSV's is surprising since these are the final products to form. The dealkylation of the naphthalenes followed the same trend as the alkylbenzenes--methyl-naphthalene went through a maximum and then decreased at higher temperatures.

In methanol conversion, the partial pressure of the feed has a major effect on the product distribution with low partial pressures leading to lower yields of aromatics since they are formed by the polymerization of the alkenes (7). The effect of increasing the partial pressure of feed on the product distribution from the conversion of biomass pyrolysis products may not be the same as with methanol since the aromatics possibly form in a different mechanism. The work reported in this paper is at low partial pressure of wood pyrolysis vapor in helium (1% by volume, assuming a vapor molecular weight of 100). Variation of this parameter remains to be studied and could provide crucial insight as to the mechanisms of both olefin and aromatic production in wood pyrolysis product conversion.

This screening technique is not the optimum method of addressing yields of hydrocarbons based on the initial weight of wood, but an experiment was performed to estimate the yield of organic products, to put the screening results in perspective. Table 1 shows estimates of the wt % of products based on the relative sensitivities of the major products in this mass spectrometric detection method. The vapors analyzed include the moisture in the feed and the water, CO, and CO<sub>2</sub> generated in the primary pyrolysis of the wood. Yields were estimated by correcting the composition of the vapor for coke deposition on the catalyst and the char from the initial pyrolysis. The coke was determined by weighing the catalyst before and after a known amount of wood was pyrolyzed and passed over the catalyst. The resulting estimates of the yield of organics varied from 8% to 11%, depending on the temperature and WHSV. Since the stoichiometry of wood can allow a potential yield of 30% light aromatics from wood due to the removal of oxygen as H<sub>2</sub>O and CO (4), the 11% hydrocarbon yield represents 30% of the theoretical yield of hydrocarbons from wood. For additional stoichiometric constraints on aromatic yields, see Diebold and Scahlil (4) in this symposium.

The relatively low levels of hydrogen in biomass, coupled with the high amount of oxygen to be rejected, are the reason for the 30% theoretical yield of hydrocarbons. This has led Chen et al. (8) to propose the cofeeding of methanol with carbohydrates to enrich the feedstock in hydrogen and increase the potential hydrocarbon yield. This idea was briefly explored with wood, and the product distributions are shown in Figure 3 for methanol, wood, wood-plus-methanol, and wood-plus-methanol with the methanol contribution subtracted. As in Figure 1, the peaks for water (m/z 18), CO (m/z 28 [also in part due to ethylene]) and CO<sub>2</sub> (m/z 44) are under-represented in these spectra due to the tuning of the mass spectrometer. The product distribution for methanol conversion at 500°C and WHSV = 2.8 (Figure 3A) shows the major classes of products: dimethyl ether (m/z's 45 and 46); the alkenes (m/z's 28 [also in part due to CO], 42, 56, 70, and 84); and the methylated benzenes (m/z's 92, 106, and 120). Alkanes are also a major product from methanol conversion but are not prominent in the runs spectra due to lower ionization sensitivity and increased ionization fragmentation. The peaks at m/z's 147 and 162 are due to penta and hexamethylbenzene, which form in high abundance when methanol is run immediately after wood, possibly due to alkylation of coke precursors and stripping from the catalyst surface. The aspen product distribution at 500°C and WHSV = 1 (Figure 3B) has similarities to the methanol, including the presence of the olefins (m/z's 28, 42, and 56) and the light aromatics. When the

Table 1. Estimated Product Yields from MBMS Data

Temp, °C WHSV, hr <sup>-1</sup>	450	450	510	500	495
	2.4	4.2	2.7	3.6	4.0
Water, wt % of Vapors	63.8	50.6	45.3	49.5	50.7
CO, wt % of Vapors	10.7	19.1	23.8	19.8	18.7
CO <sub>2</sub> , wt % of Vapors	14.5	18.4	16.4	17.0	15.6
Olefins, wt % of Vapors	6.9	6.3	10.3	8.8	9.7
BTX, wt % of Vapors	3.0	4.0	3.3	3.9	4.2
Sum of Organics, wt % of Vapors	11.0	11.9	14.6	13.6	15.0
Sum of Inorganics, wt % of Vapors	89.0	88.1	85.4	86.4	85.0
Yield of Organics, wt % of Wood	8.0	8.7	10.7	9.9	11.0

two are run together, the spectrum looks fairly additive with lesser amounts of olefins than in the pure methanol (Figure 3C). When the methanol contribution is subtracted from the combined run (Figure 3D), it is apparent that the yield of aromatics from the biomass components is increased due to the presence of methanol, and the distribution of products has changed with more xylene and trimethylbenzene, relative to benzene and very little alkenes. The methylation of the biomass-derived aromatics is not only increasing the yield beyond the addition of the two contributions, but is also changing the products toward higher value components. Based upon the GC analysis of the noncondensable gases (4), this increase in methylated benzenes would be expected to occur at the expense of the gaseous alkanes formed from pure methanol.

The behavior of model compounds, in a very preliminary screening, has given some insight toward potential yields. The product spectra of four model compounds are shown in Figure 4. These spectra were collected under different tuning conditions than previous results to bring up the low masses. As with Figures 1 and 2, however, these results have not been calibrated, so peak heights are not directly interpretable as yields. The best use of these model compound screening results is for product slate comparisons. The two major trends are summarized here: (1) the carbohydrate-derived ring compounds such as  $\alpha$ -angelicalactone (Figure 4B) and furfuryl alcohol gave the greatest yields of aromatics, while lower yields were obtained from the light oxygenates, such as hydroxyacetaldehyde (Figure 4D); and (2) lignin-derived products, from catechol and guaiacol to isoeugenol (Figure 4A) and coniferyl alcohol, gave very low yields of light aromatics and total organics but were completely destroyed, indicating a high coking potential for the lignin-derived methoxyphenols and phenols.

The formation of furan from cellulose was previously reported (9). Furfural formed furan as shown in Figure 4C; methyl furfural formed mostly methyl furan with minor amounts of furan; and hydroxymethyl furan formed more furan than methyl furan.

The yield of water was always greater than the sum of CO and CO<sub>2</sub> for both the lignin and the carbohydrate products that were studied except for the carbohydrate ring compounds such as  $\alpha$ -angelicalactone and furfural. Several compounds gave high yields of particular products that were more related to the functionality than the elemental composition: (1) compounds containing aldehyde groups, such as hydroxyacetaldehyde (Figure 4D) and the furfurals (Figure 4C), gave higher yields of CO (Angelicalactone also gave high yields of CO), (2) acetic acid gave a relatively high abundance of CO<sub>2</sub> as might be expected due to decarboxylation, (3) acetic acid and acetol gave high relative yields of alkenes relative to the heavier compounds, perhaps due to the formation of C<sub>2</sub> and C<sub>3</sub> hydrocarbons after the loss of oxygen as H<sub>2</sub>O or CO<sub>2</sub>, and (4) hydroxymethylfurfural gave less than half the yields of all organic products than did methyl furfural.

In addition to selected model compounds, three carbohydrates were pyrolyzed and passed over the catalyst. Levoglucosan, glucose, and sucrose gave the same distribution of product classes.

#### SUMMARY

The results obtained so far with wood vapor over Mobil's sample of HZSM-5 can be summarized as follows:

- Yields of total organics up to 30% of a postulated theoretical maximum yield of 30 wt % have been obtained.

- H<sub>2</sub>O always exceeds the sum of CO and CO<sub>2</sub> for wood vapor products.
- Yields of olefins exceed those of aromatics, quite probably due to the low partial pressure of wood vapor in He (typically 1 vol % assuming a wood vapor average molecular weight of 100).
- Fresh catalyst is extremely active, converting all wood-derived species, even heavy lignin species, although coke is a likely major product.
- Methanol (approximately 1.5:1 methanol/wood pyrolysis vapor by weight) increased the hydrocarbon yield, mainly as xylene and trimethylbenzene.
- Product slates can be manipulated by temperature and WHSV.
- There are virtually no intermediates observed from wood vapors (as with dimethyl ether from methanol), except furan species from the carbohydrates.

It is apparent that in future work, catalyst characteristics and variations such as surface acidity, crystallite size, and Si/Al ratio should be explored. In addition, model compounds should be studied to explore the mode of oxygen removal and coking in functionalities present in wood vapor. The synergistic benefits of methanol as a hydrogen carrier should be quantified.

#### ACKNOWLEDGEMENTS

The support of the Biofuels and Municipal Waste Technology Division of DOE, through Si Friedrich, Gary Schiefelbein, and Don Stevens, is gratefully acknowledged (FTP 646).

#### REFERENCES

- (1) Pacific Northwest Laboratory, Battelle, "Proceedings of the 1985 Biomass Thermochemical Conversion Contractors' Meeting," October 15-16, 1985, Minneapolis, PNL-SA-13571, CONF-8510167, February 1986.
- (2) Pacific Northwest Laboratory, Battelle, "Biomass Thermochemical Conversion Program Review," 2nd Quarter, FY 85, DOE/BETD, Washington, D.C. (1985).
- (3) Diebold, J. P.; and Scahill, J. W., "Production of Primary Pyrolysis Oils in a Vortex Reactor." See paper in this symposium.
- (4) Diebold, J. P.; and Scahill, J. W., "Biomass-to-Gasoline (BTG): Upgrading Pyrolysis Vapors to Aromatic Gasoline with Zeolite Catalysts at Atmospheric Pressure." See paper in this symposium.
- (5) Samples of ZSM-5 kindly supplied through Gus Weiss, Mobil Research and Development Corporation, Princeton, New Jersey (catalyst designated MCSG-2) (1986).
- (6) Evans, R. J.; and Milne, T. A., "Molecular Characterization of the Pyrolysis of Biomass. I. Fundamentals," to appear in *Energy and Fuels*, 1987.
- (7) Chang, C. D., "Hydrocarbons from Methanol," 1983, Marcel Dekker, Inc.: New York.
- (8) Chen, N. Y.; Degman, T. F.; and Koenig, L. R., "Liquid Fuel from Carbohydrates," *Chemtech*, 1986, pp. 506-511.
- (9) Diebold, J. P.; Chum, H. L.; Evans, R. J.; Milne, T. A.; Reed, T. B.; and Scahill, J. W., "Low Pressure Upgrading of Primary Pyrolysis Oils from Biomass and Organic Wastes," IGT/CBETS Conference on Energy from Biomass and Wastes, X, Washington, D.C., April 7-10, 1986.

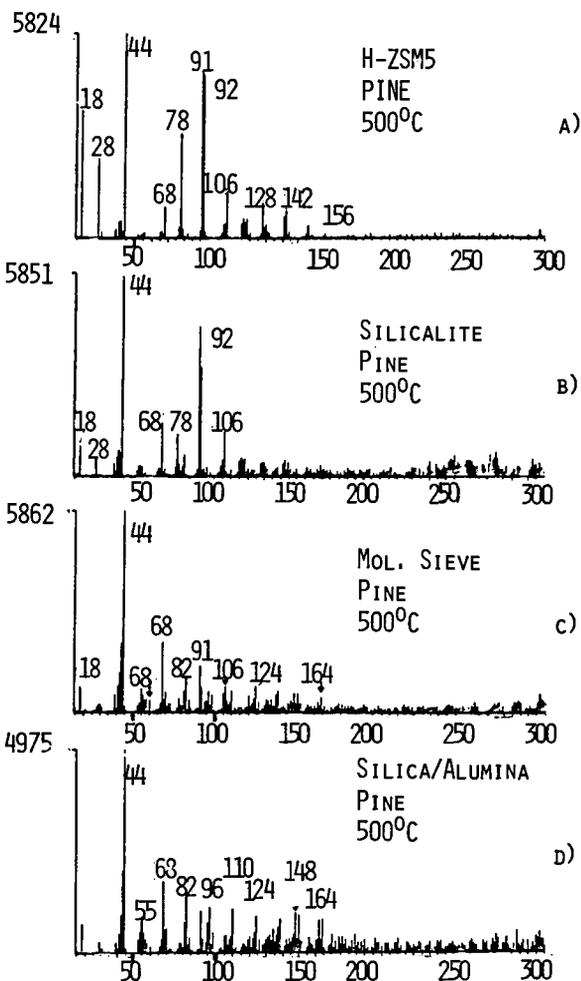


FIGURE 1. MASS SPECTRA OF THE PRODUCTS OF THE CONVERSION OF PINE WOOD PYROLYSIS VAPOR OVER VARIOUS CATALYSTS AT 500°C AND WHSV OF 1: A) MOBIL'S HZSM-5; B) UNION CARBIDE'S SILICALITE; C) UNION CARBIDE'S MOLECULAR SIEVE; AND D) DAVIDSON'S SILICA/ALUMINA.

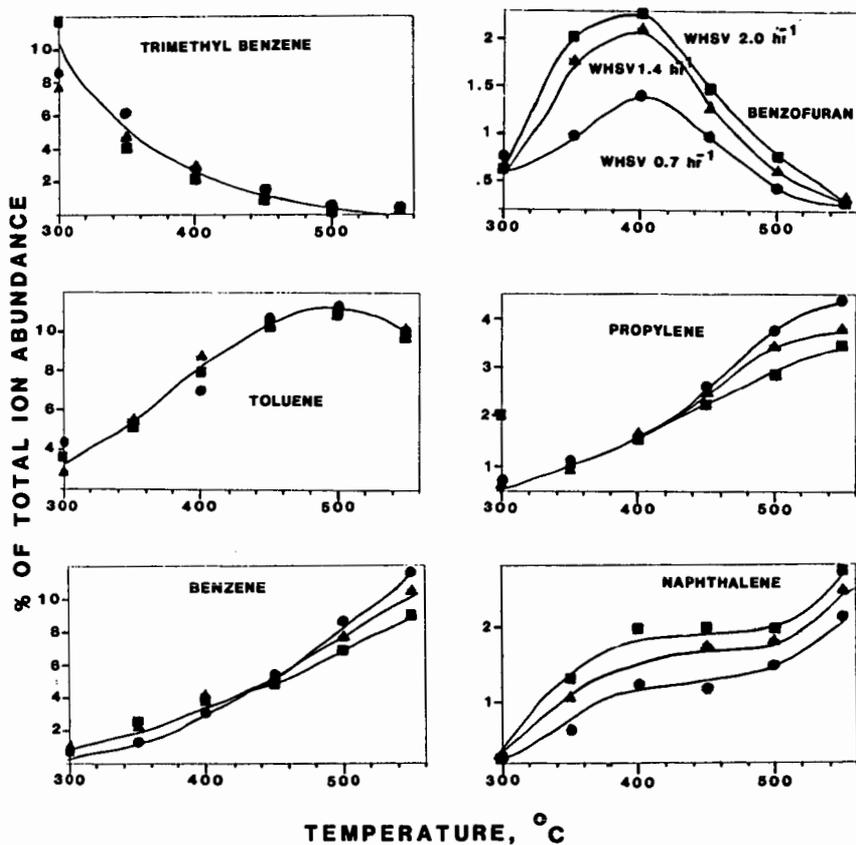


FIGURE 2. THE EFFECT OF TEMPERATURE AND WHSV ON THE DISTRIBUTION OF PRODUCTS FROM THE CONVERSION OF PINE WOOD PYROLYSIS VAPORS OVER H-ZSM5 CATALYST. NOTE: % OF ION ABUNDANCE SHOULD NOT BE EQUATED WITH % OF NEUTRAL PRODUCTS SINCE MASS SPECTROMETER TUNING AND CROSS SECTIONS FAVOR AROMATICS.

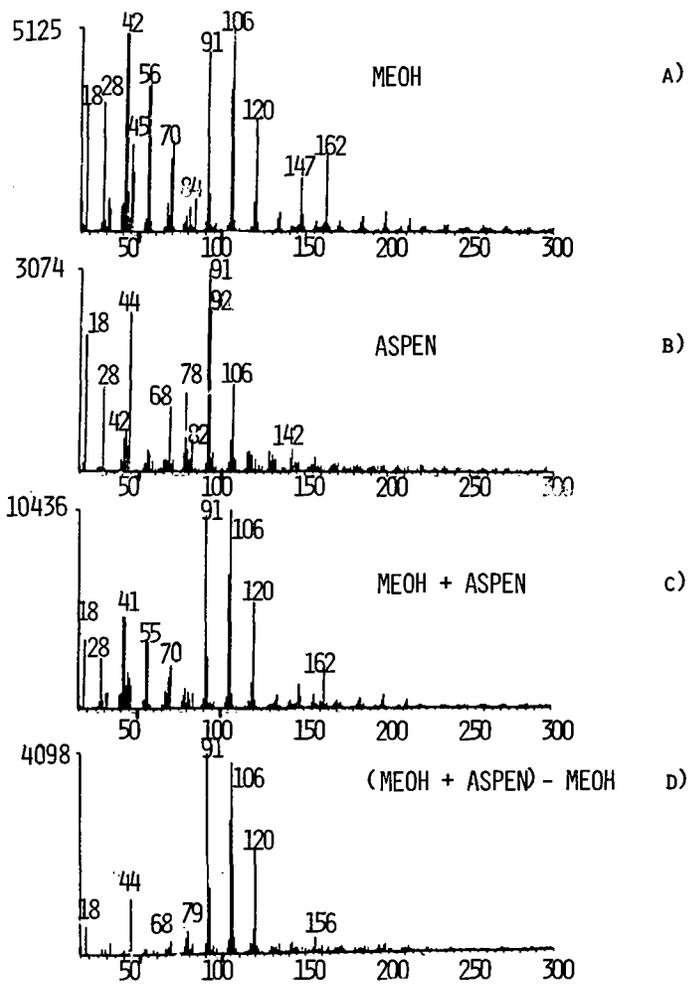


FIGURE 3. MASS SPECTRA OF THE PRODUCTS OF THE CONVERSION OF METHANOL AND ASPEN PYROLYSIS VAPORS OVER HZSM-5: A) METHANOL ALONE, 500°C, WHSV = 2.8; B) ASPEN PYROLYSIS PRODUCTS ALONE, 500°C, WHSV = 1.9; C) COFEEDING METHANOL AND WOOD USING THE CONDITIONS IN A) AND B); D) THE RESULTS IN C) WITH THE METHANOL ALONE RESULTS A) SUBTRACTED SHOWING THE ENHANCEMENT TO THE ASPEN PRODUCT DISTRIBUTION.

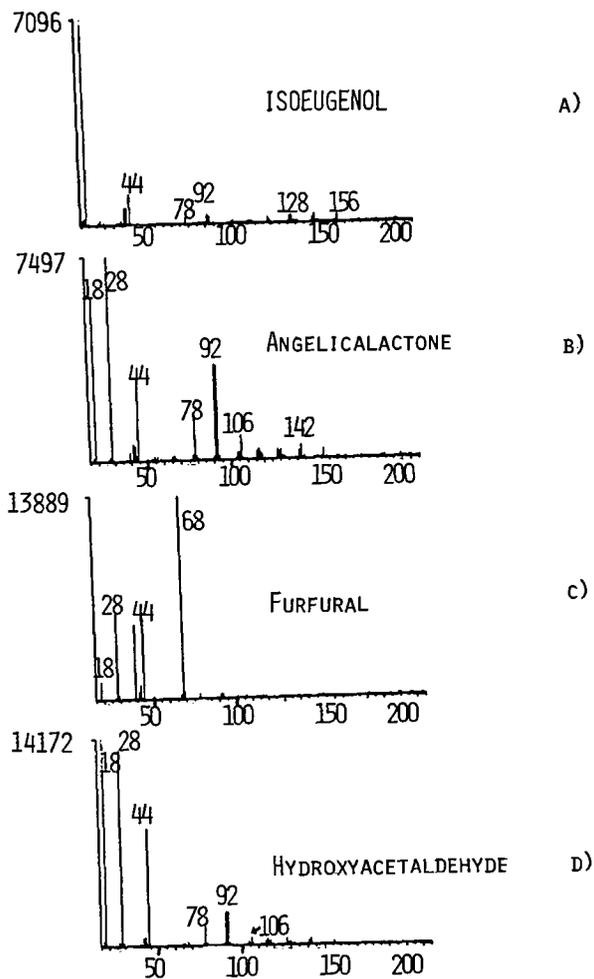


FIGURE 4. MASS SPECTRA OF THE PRODUCTS OF THE CONVERSION OF MODEL COMPOUNDS OVER HZSM-5: A) ISOEUGENOL, 500°C, WHSV = 2.4; B)  $\alpha$ -ANGELICALACTONE, 500°C, WHSV = 2.0; C) FURFURAL, 500°C, WHSV = 1.5; AND D) HYDROXYACETALDEHYDE, 500°C, WHSV = 6.1.