

Lignin Derivatives Formation In Catalysed Thermal Decomposition Of Elephant Grass Lignocellulose

K.I. Ekpenyong,* E. A. Clement, O.S. Olatunde and N.Obi
Department of Chemistry, University of Jos, PMB 2084 Jos, Nigeria

ABSTRACT

*Decomposition of elephant grass (Panicum maxima) lignocellulose was carried out with Pd and Ni/Pt-doped alumina as catalysts; chromic oxide was also used in some cases. For systems that contained no chromic oxide, formation of gaseous and volatile liquid products was highest for Ni/Pt, intermediate for Pd/ λ - and least for Pd/ γ -alumina. Non-volatile (tar) liquid product formation, on the other hand, was highest for Pd/ λ -, intermediate for Pd/ γ - and least for Ni/Pt-alumina. In these systems, product formation in detectable and measurable amounts was first observed at 140°C. For systems that contained chromic oxide, product formation was first observed at 60°C. The order of reactivity of the catalysts was Ni/Pt- > Pd/ λ - > Pd/ γ - alumina for the gaseous and Pd/ γ - > Pd/ λ - > Ni/Pt-alumina for the volatile liquid products in the range of 100 – 140°C. For the non-volatile (tar) liquid products, the order was Pd/ γ - > Pd/ λ - > Ni/Pt-alumina in the range of 60 - 80 °C and Pd/ γ - > Ni/Pt- > Pd/ λ - alumina at 100 – 120°C. Generally, gaseous and volatile liquid products increased with increase in temperature. Also, all the three product types were formed in significantly higher concentrations in systems without chromic oxide than those with it. Mass spectral analysis of the tar product of two Ni/Pt-alumina samples run at 180°C and 200°C without chromic oxide gave several products among which 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3, 5-dimethylbenzaldehyde, 3-isobutyl-4-hydroxy-5-methoxybenzaldehyde, 3-methoxycinnamic acid, and ethanone-1(4hydroxy-3-methoxyphenyl) were identified. * Author for correspondence*

INTR ODUCTION

Biomass in the form of household, municipal, industrial and agricultural wastes will continue to play an important role in the generation of energy, fuels and chemicals. Biomass is relatively abundant and renewable, and this makes it particularly attractive in relation to the non-renewable fossil fuels.

For the past several years, we have been engaged in the biochemical and thermochemical conversion of grasses and

straws, in particular sorghum straws and the elephant grass¹⁻³. A vast expanse of grassland extends far and wide, north and south of the equator in the savannah region of the African continent. Some of this is used as pasture, the dry material as fuel and roofing material in home construction, but the bulk of the dry material is flared away, usually in preparation of the land for the next planting season. These grasses and straws constitute an enormous energy resource. From all indications⁴, it is apparent that a combination of biochemical and thermochemical methods would

definitely be needed to maximally tap the energy potentials of these grasses and straws. Thermochemical methods such as pyrolysis and gasification can be regulated to generate liquid fuels, particularly by the process of catalysis with controlled temperature conditions.

The composition of grasses and straws is largely lignocellulosic^{5,6}. For the stems of monocotyledons, grasses, bamboos, wheat, rice and sugar cane, Katzen⁵ reports the following compositional ranges: cellulose (25-40%); hemicellulose (25-50%); lignin (10-30%). In the case of wheat straw, Scott and co-workers⁶ report the following: cellulose (32.4%); hemicellulose (41.8%) and lignin (16.7%). These values are well within the Katzen ranges. The cellulose and lignin compositions of the elephant grass, the focus of the present study, can be expected to lie within the given ranges.

Pyrolysis of agricultural wastes has been reported abundantly in the literature.⁷⁻¹¹

Kaminsky¹² has discussed in great detail the existing pyrolytic methods including detailed product compositions of pyrolysed biomass materials.

Thermocatalytic biomass decomposition has also been reported¹³⁻¹⁵. Chen¹³, for example, observed a decrease in the heat of gasification and mass fraction of non-combustible volatiles in solid NaOH-catalysed thermal decomposition of pure and fire-retardant-cellulose. Kuroda and co-workers¹⁴ studied the Curie-point pyrolysis of Japanese softwood species of the red pine, cedar and cypress in the presence of inorganic substances. The studies were carried out in the temperature range of 358-764°C with the goal of obtaining larger yields of lignin-derived products. The Al-Cu-Cr oxide system has been used as a catalyst in fluidized bed thermal decomposition of

wood lignin; high quality carbon was produced while harmful pyrolysis products were eliminated¹⁵. These examples illustrate the potentials of catalyzed pyrolytic biomass decomposition. Evidently¹³, biomass thermocatalysis does not only cause the lowering of the reaction temperature but can also be employed to selectively obtain desired products among gases, volatile and non-volatile liquids. Pyrolysis of the various plant materials has been shown to give high yields of liquid products¹⁶. Pyrolysis tars, which contain oxygenated liquids in addition to regular hydrocarbons, can become important gasoline blends in the current efforts to reduce pollution resulting from sulphur oxide emissions of fossil fuels.

Because of the importance currently being attached to pyrolytic tar products, we undertook in the present study to also determine the kinds of chemical compounds contained in such products.

EXPERIMENTAL

Samples

Elephant grass samples used for the present study were obtained from the University of Jos surroundings. These comprised the plant stalk, cut above the roots. These were chopped into small pieces, washed, oven-dried at 100°C for two hours, cooled and ground to < 250µm mesh size.

Sample extraction

Each sample so treated was next extracted by the method of Crawford¹⁷ in order to remove the protein and carbohydrate components. The sequential extraction was first with water, next with

benzene-ethanol mixture (1:1,v/v), followed finally by each of ethanol and water, respectively. Each extraction was for 30 minutes at 80°C. The soxhlet extractor was used. The resultant residue was oven-dried for 48 hours at 105°C. The final product was stored in a desiccator until needed for further use.

Catalysts

The catalysts had the following compositions: 0.5% for Pd and 1.0% for each of Ni and Pt. Alumina of the λ and γ types were used. Their Pd and Ni/Pt dopes as Pd/ λ -, Pd/ γ - and Ni/Pt- were used directly as obtained from the manufacturers.

The reactor and heating system

The reactor consisted of pyrex tubes of 16cm length and 1.5cm internal diameter. The heating medium was a cylindrical brass block of 9cm height and 7cm diameter into which three thermal wells were drilled at approximately equal distance apart. Each well had a depth of 7cm and 1.7cm diameter,

The pyrolysis sample

For a typical run, each tube was charged with the predetermined amount of lignocellulose (LC) or the LC/catalyst/Cr₂O₃ blend. Each charge contained 1-2g LC and 40mg catalyst. For systems that contained chromic oxide, a blend of LC/Cr₂O₃ (1:2, w/w) was used. After each loading, the open end of the tube was narrowed by drawing a capillary. A small piece of cotton wool was next inserted at the capillary end and the tube evacuated to a pressure of about 1mm Hg. On removal of the cotton wool, the tube was sealed by means of a butane/oxygen flame.

The pyrolysis and product recovery

The samples, now contained in the sealed and evacuated tubes, were next inserted into the preheated thermal wells. Each sample was pyrolysed for 2h; the pyrolysis temperature varied between 60° and 200°C. At the end of each run the tubes were cooled and then cracked open, thereby allowing the gaseous products to escape.

The gaseous products

The difference in weight of the evacuated and sealed tube prior to pyrolysis and the cracked open tube (glass pieces included) gave the collective weight of the gaseous products.

Non-volatile and volatile liquid fractions

The residual reactor material was soxhlet –extracted in benzene for 72 h. This gave the weight of the non-volatile (tar) liquid (NVL) product. By mass balance of gaseous, non-volatile liquid, residual material after soxhlet extraction, the weight of the volatile liquid (VL) fraction could be determined.

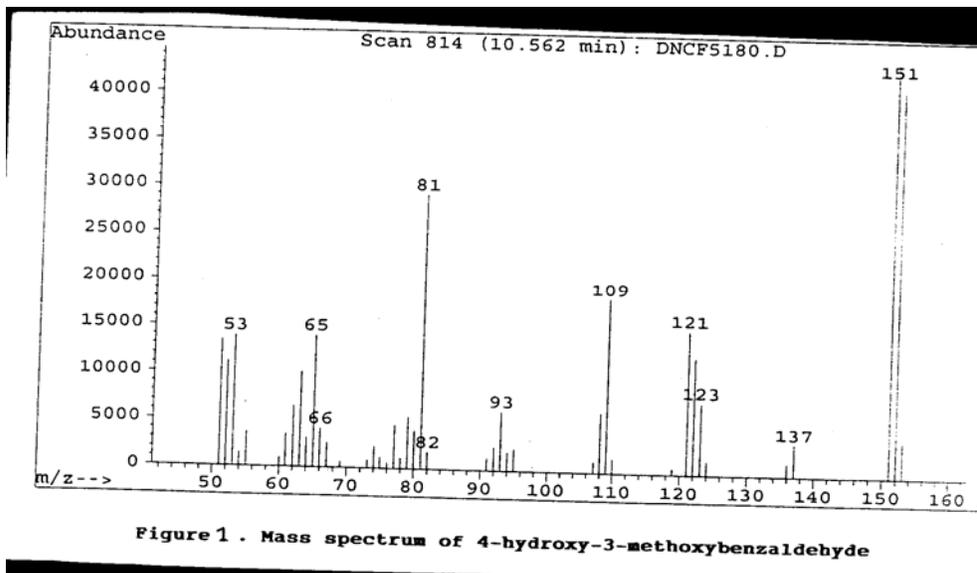
Analysis of NVL fractions for components

In addition, the benzene-extracted NVL fractions of LC/Ni/Pt- Al₂O₃, run at 180°C and 200°C, without chromic oxide, were analyzed by GC/MS for their chemical constituents. These low retention mass spectra were recorded on the Hewlett-Packard 5890 GC, equipped with a flame ionization detector and the Hewlett-Packard 5972 mass selective detector. The compounds were identified with the help of the Wiley 138.L Database

RESULTS AND DISCUSSION

Tables 1 and 2 show, respectively, the results of the computational analysis for the products (gases, volatile and non-volatile liquids) of systems that contained chromic oxide and those that did not. In Figures 1-5, the mass spectra of the tar

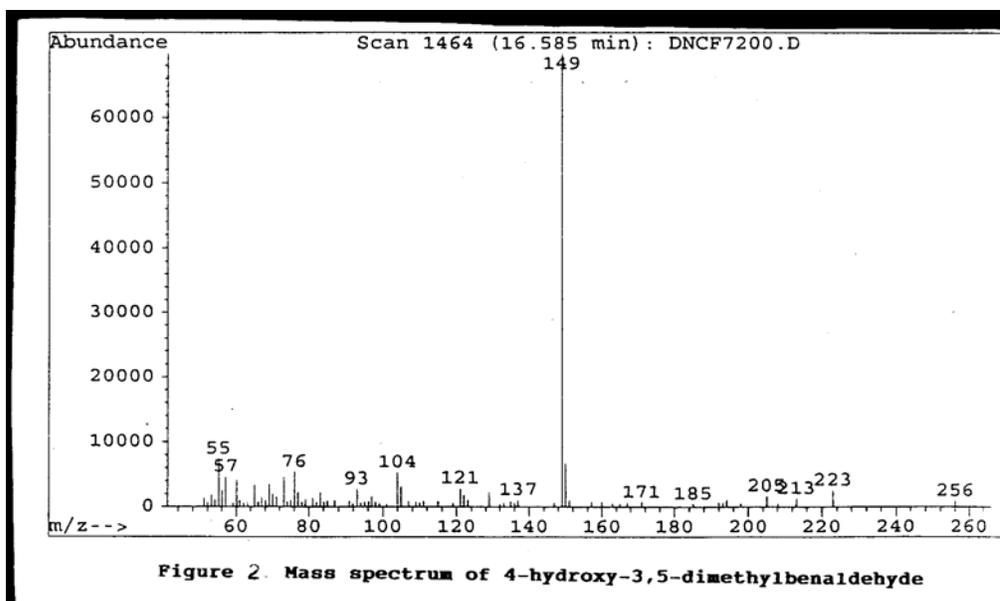
products, identified as 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3, 5-dimethylbenzaldehyde, 3-methoxycinnamic acid, ethanone-1 (4-hydroxy-3-methoxyphenyl) and 3-isobutyl-4-hydroxy-5-methoxybenzaldehyde are presented.



Systems without Cr₂O₃

Preliminary studies with lignocellulose (LC) alone showed that products formation in measurable quantities did not occur below 180°C. The first determinable product mixture was obtained for runs carried out at 180°C and in the 180°C to 200°C range the amount of product formed was relatively small.

When the various catalysts were added to LC, products were formed in measurable quantities at a temperature as low as 140°C. The gaseous and volatile liquid products increased quantitatively with increase in temperature; the non-volatile liquids, on the other hand, decreased with increase in temperature (Table 1)



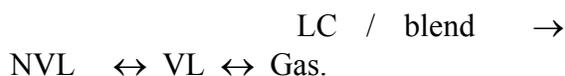
Systems with Cr₂O₃

With LC/Cr₂O₃ without the catalysts, products were first obtained at 80°C. When the various catalysts were added, product measurement was possible starting at as low as 60°C. Noteworthy in these systems also is that while the concentrations of gaseous and, to some extent, volatile liquid products were significantly higher, those of the non-volatile liquid products were considerably lower than those of systems without Cr₂O₃ (compare Tables 1 and 2 at 140 °C).

The results of Tables 1 and 2 provide the following classification of the activity of the catalysts: Ni/Pt- > Pd/λ - > Pd/γ - Al₂O₃ in the formation of gaseous and volatile liquid products in the systems without chromic oxide. Similarly, for the NVL the order was Pd/λ > Pd/γ - > Ni/Pt- Al₂O₃. For systems containing chromic oxide, the catalyst order of activity was found to be Ni/ Pt - > Pd/ λ - > Pd/ γ - alumina for the gaseous products; Pd/ γ - > Pd/ λ - > Ni/ Pt - for the volatile liquids in the range of 100° - 140 °C. For the NVL the order was Pd/ γ - > Pd/ λ - > Ni/ Pt - in

the range of 60 - 80°C and Pd/ γ - > Ni/Pt - > Pd/ λ - alumina at 100 - 120 °C.

Generally, volatile and gaseous products increased in quantity with increase in temperature; non-volatile liquids, on the other hand, decreased with increase in temperature. The preponderance of the gaseous and VL products at the higher temperatures and the corresponding decrease in the NVL makes the following reaction scheme plausible.



The transitions associated with this reaction scheme are temperature dependent. The results of Tables 1 and 2 show Ni / Pt- Al₂ O₃, a multi- functional catalyst, to be a good candidate for the formation of gaseous products in lignocellulose decomposition. Pd / λ - and Pd / γ - Al₂ O₃, on the other hand, are well suited to the production of VL and NVL. Bi -functional and multi-functional

Table 1: Product Yields (%) of Systems Without Cr₂O₃

Sample	Gases				Volatile Liquids (VL)				Non-Volatile Liquids (NVL)			
	140°C	160°C	180°C	200°C	140°C	160°C	180°C	200°C	140°C	160°C	180°C	200°C
0	-	-	3.0	3.5	-	-	7.3	8.3	-	-	2.5	3.5
1	10.9	17.1	21.0	26.0	8.2	9.6	13.4	18.2	19.5	16.4	12.7	7.3
2	12.7	19.5	24.3	33.2	7.7	11.3	15.5	23.2	21.3	18.7	15.3	12.5
3	17.1	27.4	31.0	36.9	14.8	19.5	24.0	24.0	18.5	15.8	11.7	8.1

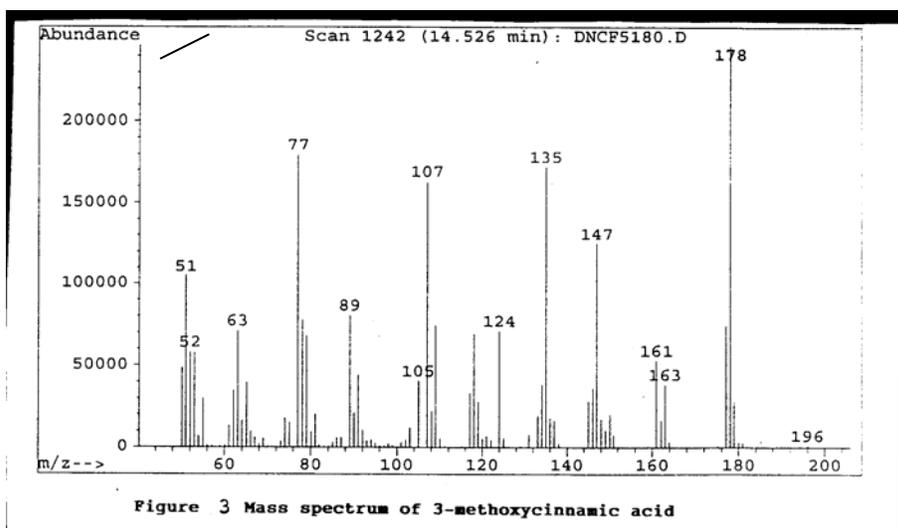
O = LC only; 1. LC + Pd/γ - Al₂O₃; 2. LC - pdλ - Al₂O₃; 3. LC + Al₂O₃

Table 2: Product Yields (%) of Systems Containing Cr₂O₃

Sample	Gases				Volatile Liquids (VL)				Non-Volatile Liquids (NVL)						
	60°C	80°C	100°C	120°C	140°C	60°C	80°C	100°C	120°C	140°C	60°C	80°C	100°C	120°C	140°C
0	-	1.0	1.4	1.6	1.8	-	3.0	3.8	4.5	4.7	-	0.4	0.3	0.3	0.3
1	4.2	5.6	6.8	9.1	11.9	4.5	5.5	7.1	9.5	10.3	17.8	15.2	10.3	8.8	6.1
2	9.1	10.6	12.8	15.2	17.8	1.6	3.7	6.4	8.8	11.8	14.2	12.3	8.8	6.7	4.8
3	10.2	12.1	14.2	16.7	19.4	3.1	4.0	4.9	8.5	8.6	11.6	11.0	9.9	8.7	4.4

O = LC only; 1. LC + Pd/γ - Al₂O₃; 2. LC - pdλ - Al₂O₃; 3. LC + Al₂O₃

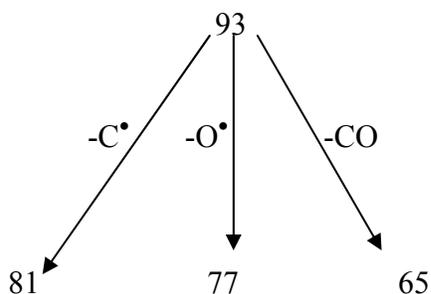
catalysts have been studied quite extensively¹⁸



and are already being employed widely in industry. The results of our present studies can be quite important in the present strong interest for liquid fuels from biomass.

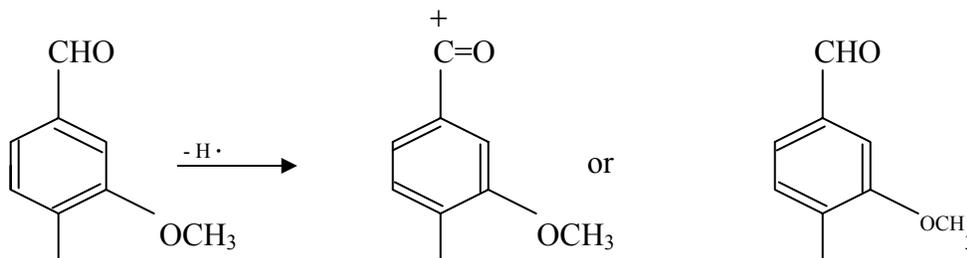
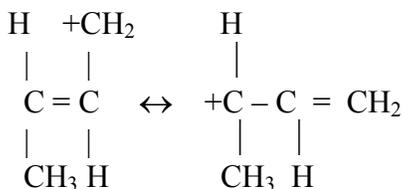
A meaningful interpretation of the mass spectra (Figures 1 – 5) requires reference to the structure of lignin, and specifically lignocellulose. Such structures have been proposed.^{19, 20} Figure 1 shows the mass spectrum of the compound identified as 4-hydroxy-3-methoxybenzaldehyde, of molecular

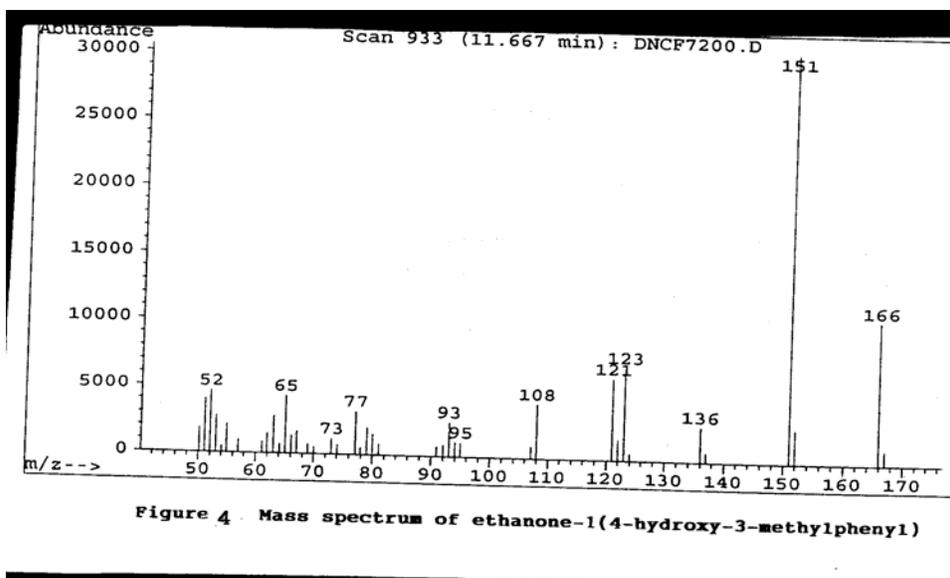
weight 152. It has an (M+1) peak of low intensity (m/e 153) and an (M-1) peak, which is the base peak (m/e 151). Some of its most significant ion fragment peaks are accounted for in the scheme presented. Mass fragment peaks at m/e 122 and 121 are formed by the successive loss of an H atom from the m/e 123 ion fragment. Similarly, the peaks at m/e 81, 77 and 65 are formed from the m/e 93 fragment as follows:



Peaks below m/e 65 are due to either lower cyclic or open chain structures. A fragment peak at m/e 55 (not labeled) is commonly associated with the

methylallylation which is quite stable. The m/e 53 could easily be formed from this fragment by loss of two hydrogen atoms.





The mass spectrum of Figure 3 is that of 3-methoxycinnamic acid of molecular weight 178. It has an (M+1) peak at m/e 179 and an (M-1) at m/e 177, both having intensities characteristic of an aromatic ether.²¹

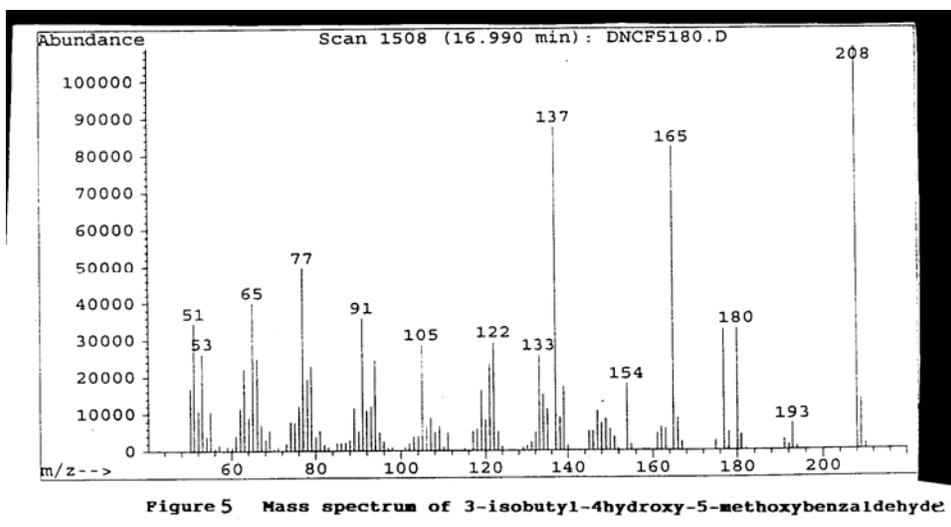
Figure 4 represents the mass spectrum of ethanone-1 (4-hydroxy-3-methoxyphenyl) of molecular weight 166. It has an (M+1) peak at m/e 167.

Figure 5 shows characteristically, a substituted benzene ring, which has been identified as 3-isobutyl-4-hydroxy-5-methoxybenzaldehyde, of molecular formula $C_{12}H_{16}O_3$ and weight of 208.

Formation of the various fragment peaks of Figures 2 – 5 can be established in the manner already discussed for Figure 1.

Noteworthy in all five compounds is the similarity in the locations of peaks characteristic of certain fragment ions that

are common to them. This is particularly true of the three compounds with the benzaldehyde unit. Furthermore, the lignin polymer contains polyphenylpropanoid units. Much of the phenyl propane monomer structure of lignin is therefore retained in these reactions as evident from the structures of the compounds reported here and such observations have been made previously.²² The performance of the three alumina-supported metal catalysts with and without Cr_2O_3 is novel in this study. Lignocellulose decomposition and product formation in sizeable quantities occur at remarkably low temperatures. While the presence of Cr_2O_3 has the effect of temperature lowering and higher yields of the gaseous and, to some extent, liquid products, it leads also to a drastic reduction in the amounts of the non-volatile liquid products formed.



CONCLUSION

The diversity of activity of alumina-supported Pd and Ni/Pt catalysts has been demonstrated in the decomposition of elephant grass lignocellulose. While Ni/Pt-alumina strongly favours gaseous product formation, Pd/ γ - and Pd/ λ - alumina strongly favour the formation of volatile and non-volatile liquid products.

ACKNOWLEDGEMENTS

This work was supported by the University of Jos Senate Research Grant no. RGC/1996/97/00010. We also acknowledge the technical support of the Department of Chemistry, the University of Florida at Gainesville, Florida, USA, for the running of the GC/MS spectra, and that of the Institute of Industrial and Petroleum Chemistry, the Technical University of Aachen, Germany, for providing the catalysts.

REFERENCES

1. Ekwenchi, M.M., Araka, B.E. and Ekpenyong, K.I., *Ind. Eng. Chem. Res.* 27(1988) 2169.
2. Ekwenchi, M.M., Akunwanne, B.U., Okeke, N.R. and Ekpenyong, K.I., *Fuel* 69(1990) 1569.
3. Ekpenyong, K.I., Arawo, J.D., Melaiye, A., Ekwenchi, M.M. and Abdullahi, H.A., *Fuel* 74 (1995) 1080.
4. Grohmann, K., Wyman, C.E. and Himmel, M.E., in Rowell, R.M., Shultz, T.P. and Narayan, R., eds., *Emerging Technologies for Materials and Chemicals*, ACS Symposium series 476, 1992.
5. Katzen, R., *ACS Symposium on Biomass as a Non-fossil Fuel Source*, ACS, Washington, D.C., 1979.
6. Scott, D.S., Piskorz, J. and Radlein, D., *Ind. Eng. Chem. Process Des. Dev.* 24(1985) 581.
7. Antal, M.J., in Klass, D.L., ed., *Energy from Biomass and Wastes*, Wiley, Chicago, 1978.
8. Appel, H.R., Fu, Y.C., Friedman, S., Yovorosky, P.M. and Nender, L., *Converting Organic Wastes to Oils*, in US

- Bureau of Mines, Report of Investigation no. 7560, 1971.
9. Diebold, J.P., ACS Symposium on alternative feedstock for petrochemicals, ACS, Div. of Petrochemistry, Las Vegas, 1980.
 10. Waterman, W.W., ACS Symposium, Orlando, FL, 1976.
 11. Kuester, I.L., ACS Symposium on biomass as a non-fossil fuel source, Honolulu, Hawaii, 1979.
 12. Kaminsky, W., Chem. Ing. Tech. 61:10 (1989) 775.
 13. Chen., Y., Chem. Abstr. 113(1990) no. 61522v.
 14. Kurado, K., Inoe, Y. and Sakai, K., J. Anal. Appl. Pyrolysis, 18:10(1990) 59.
 15. Kunetsov, B.N. and Shchipko, M.L., Bioresource Technol. 52:1(1995)13.
 16. Nunn, T.R., Howard, J.B., Longwell, J.P. and Peters, W.A., Ind. Eng. Chem. Process Des. Dev. 24(1985)844.
 17. Crawford, D.L., Appl. Environ. Microbiol. 35(1978)1041.
 18. Gates, B.C., Catalytic Chemistry, p. 396, John Wiley and Sons Inc., New York, 1992.
 19. Sarkanen, K.V. and Ludwig, C. M., eds., Lignins, Occurrence, Formation, Structure and Reactions, p.916, Wiley – Interscience, New York, 1971.
 20. Koshijima, T. and Yaku, F., in Glasser, W.G. and Sarkanen, S., eds., Lignin, Properties and Materials, Vol. 397, p. 11, ACS, Washington, D.C., 1989.
 21. Silverstein, R.M., Bassler, G.C. and Morrill, T.C., Spectrometric Identification of Organic Compounds, p.5, John Wiley and Sons, Inc., New York, 1974.
 22. Drummond, A.R. and Drummond, I.W., Ind. Eng. Chem. Res. 35(1996)1263.

Accepted 30/12/2002
Received 6/11/2002