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Quarterly Report

on

CHARACTERIZATION OF OXIDIZED COAL SURFACES[1]

May 1988 - September 1988

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ABSTRACT

Laser mass spectra have been obtained of 2-fluoro-1-methylpyridinium (FMP) derivatized coal consistent with a prime objective of this research. This reagent, specific for the hydroxy functionality, produced major peaks at m/z 184 and 199 in the spectra of Pocahontas coal following derivatization. The peaks at m/z 199 and 184 are consistent with the spectra of alkyl phenols. FMP also formed a derivative with poly (p-vinylphenol) at m/z 212, corresponding to FMP + monomer unit.

A gas phase reactor was built in order to enhance coal derivatization. Gas phase derivatization was accomplished on model compounds.

Derivatization was carried out on Illinois #6 coal and analyzed with DRIFTS to determine the extent of derivatization. Oxidation indices of the oxidized coal decreased upon reacting with 2,4-dinitrophenylhydrazine, a derivatizing agent specific for carbonyl groups, confirming that the derivatization reaction had taken place.

I. INTRODUCTION

Oxidation of coal alters its structure and properties sufficently to impede its utilization. Methods to counteract coal oxidation could be more easily developed if the mechanism of the oxidation were better understood. Although much work has been done to characterize the oxidation processes, only limited progress has been made. This is due in part to the complex structure of coal and the subtle chemical changes that take place during oxidation. There exist many physical tests that can determine the extent of coal oxidation, however very few methods have been found to study the oxidation pathway. Some spectroscopic techniques that have proven useful in studying coal oxidation are: XPS[1] (X-ray Photoelectron Spectroscopy), DRIFTS[2] (Diffuse Reflectance Infrared Fourier Transform Spectroscopy), SIMS[3] (Secondary Ion Mass Spectrometry), and more recently LMS[4] (Laser Mass Spectrometry).

The purpose of this research is to characterize compounds containing oxygen specific functionalities formed on the surface of coal during the oxidation process. This is being accomplished using in situ derivatization reactions for specific functional groups in combination with the spectroscopic techniques of SIMS and LMS.

The general approach being used in this study is a three step process:

1. Derivatives of model compounds have been prepared and analyzed by LMS and SIMS from metal substrates.

2. Derivatives of model compounds have been prepared and analyzed by LMS and SIMS from carbonaceous substrates.

3. Coal samples have been oxidized under a variety of controlled conditions and analyzed using LMS and SIMS before and after addition of derivatizing agents.

II. EXPERIMENTAL

Work during this quarter involved: (1) Following the derivatization reactions of benzyl alcohol, poly (p-vinyl phenol), and coal by LAMMA analysis using FMP (2-fluoro-1-methylpyridinium), (2) Monitoring of the C=O streching band in coal before and after the addition of 2,4-dinitrophenylhydrazine using DRIFTS, (3) Construction of a gas-phase derivatization unit and its use on model compounds and on coal.

PREPARATION OF 2-FLUORO-1-METHYLPYRIDINIUM DERIVATIVES (FMP)

FMP derivatives were prepared according to the procedure described by Mukaiyama[5]. The FMP derivative of benzyl alcohol was analyzed by LAMMA and reported previously (see Quarterly Report for Feb., 1988 - April, 1988). In this quarter, derivatization was carried out on poly (p-vinyl phenol) and Pocahontas coal.

LMS ANALYSIS

Positive and negative ion laser mass spectra were obtained using the Leybold-Heraeus LAMMA-1000. A description of the LAMMA-1000 was provided in the Quarterly Report for Oct. 1-December 31, 1986.

DRIFT ANALYSIS

DRIFT analysis was used this quarter to determine the extent of derivatization of Pocahontas coal by monitoring the changes in its oxidation index after derivatization. Data was collected on a Digilab 15 FTIR and oxidation indices calculated using the method developed by researchers at US Steel (Fuel, 1985) and currently used at CONOCO (J. Energy and Fuels, 1988).

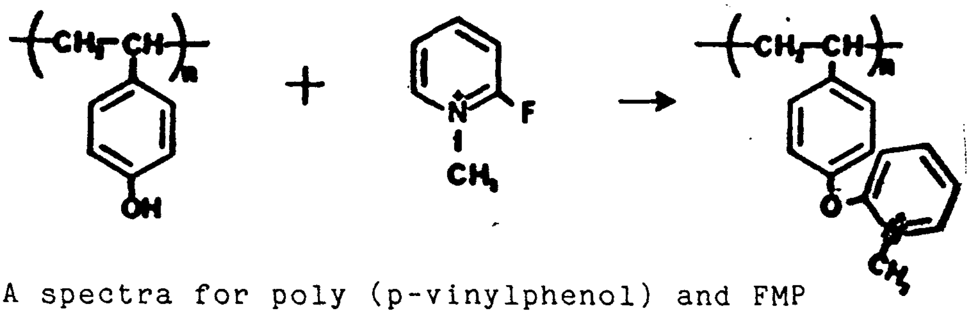
GAS PHASE REACTOR

In an attempt to increase the ease of formation of derivatization products, and to eliminate the problem of excess derivatizing agents remaining on the coal surface, a gas-phase reactor was built, similar in design to a reactor designed by Vath and Biemann for derivatization of nonvolitiles. The reactor, as seen in figure 1, is constructed of glass and consists of a reagent well, a -200 mesh screen insert on to which sample is placed, and a vacuum tight covering with an aspirator port. Derivatizing agent is placed in the reagent well, along with a magnetic stirring bar. The sample is then placed on top of a -200 mesh screen insert which sits approximately 2 cm above the surface of the derivatizing reagent. The reactor is clamped shut, a vacumm is drawn on the system using an aspirator, and the reagent well is heated close to the boiling point of the reagent using heating tape. The system is then allowed to stand for approximately 1 hour, after which time the sample is removed for analysis.

III. RESULTS AND DISCUSSION

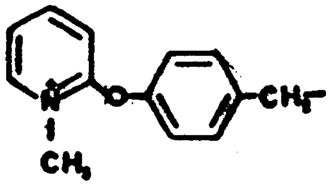
DERIVATIZATION USING FMP

Under ambient conditions, FMP can be used to derivatize phenolic compounds. As seen in the Quarterly Report for Feb., 1988 - Apr., 1988, FMP will form a derivative with benzyl alcohol that can be observed using the LAMMA. In this reporting period derivatization was carried out on a more complex phenolic compound, the polymer poly (p-vinyl phenol). The reaction of this polymer with FMP is as follows:



The LAMMA spectra for poly (p-vinylphenol) and FMP derivatized poly (p-vinyl phenol) are shown in figures 2A and 2B, respectively. A peak can be seen at m/z 212 corosponding to the repeat unit (vinyl phenol) plus FMP. A large peak can also be seen for FMP - F at m/z 93. The importance of this reaction can be seen when the LAMMA spectrum of underivatized poly (p-vinyl phenol) in figure 2A is compared with that of the derivatized polymer. The derivatization reaction leads to a much less complex spectrum, and stablizes the vinyl phenol repeat unit at m/z 120, which can barely be seen above the level of noise in the underivatized sample.

After obtaining favorable results with benzyl alcohol and poly (p-vinyl phenol), the FMP reaction was attempted on coal. The LAMMA spectrum for Pocahontas coal and Pocahontas coal + FMP is seen in figure 3. A large peak can be seen for FMP - F at m/z 93 in the derivatized coal spectrum, as well as some higher mass peaks at m/z 184 and 199 which do not occur in the spectrum of coal alone. One possible structure that could give rise to peaks at m/z 184 and 199 is the FMP derivative of a phenolic type structure present on the coal surface. The structure is as follows:



DRIFT ANALYSIS OF DERIVATIZED COAL

DRIFTS has been used by many researchers to study the extent of coal oxidation. In this quarter DRIFTS has been used to indicate the extent of derivatization of Pocahontas coal by monitoring changes in the C=O and C-H stretching bands after derivatization. Pocahontas coal was reacted with 2,4-dinitrophenylhydrazine, a derivatizing reagent which is specific for carbonyl groups. Figures 4A and 4B show the DRIFT spectra and oxidation indices for derivatized and underivatized Pocahontas coal. The oxidation index for underivatized coal has a value of 1.06 while the oxidation index of the derivatized coal decreases to 0.86, suggesting that derivatization of the carbonyl functionality has taken place. LAMMA analysis of the same derivatized sample shows no peaks which are not common to coal alone or derivatizing agent alone. This would seem to indicate that one of the biggest problems in using the LAMMA to probe derivatization reactions on the surface of coal is the stability of the derivative and the energy needed to desorb it. Possibly the energy needed to desorb the derivative from the coal matrix is enough to also cleave the reagent-functional group bond, in the case of C=O derivatizations.

GAS PHASE REACTOR

As mentioned previously, a gas phase reactor was constructed in an attempt to facilitate the formation of a derivatized product. The derivatizing agent chosen was trimethylsilazane (TMS) because of its volitility and because of the high reactivity of TMS for phenolic compounds. B-naphthol was placed in the reactor along with TMS and allowed to react for one hour, after which the sample was removed and analyzed by LAMMA. The LAMMA spectrum of TMS derivatized B-naphthol is seen in figure 5. An intense peak corresponding to the molecular ion of the derivative can be seen at m/z 216, as well as peaks representing losses of methyl groups and various lower mass fragments from B-naphthol. Upon successful use of the gas-phase reactor on a model compound, a sample of oxidized Pittsburgh Seam coal was placed in the reactor and allowed to react. LAMMA analysis of the reacted coal, however, gave no evidence that a reaction had taken place.

CONCLUSIONS

The derivatizing agents FMP and TMS have been shown to react well at ambient temperatures and produce molecular ion species upon LAMMA analysis. There is evidence that FMP formed a detectable derivatized species, indicative of a phenolic compound, when reacted with Pocahontas coal. A gas-phase reactor has been built and has shown to enhance the derivatization of model compounds. Data from DRIFTS analysis seems to indicate that derivatization of coal does take place using 2,4-dinitrophenylhydrazine, although LAMMA analysis of the product gives no information which indicates a derivatized product has formed. These findings seem to indicate that in order to use a derivatization technique combined with LAMMA analysis to study the effects of oxidation on coal, the chemical bond formed between the derivatizing agent and the oxygen containing functional group must be strong enough to withstand the amount of laser energy needed to desorb the derivatized complex from the coal matrix. There is evidence that FMP and TAB (see Quarterly Report for Feb., 1988 - April, 1988 for TAB reaction) form derivatives with surface components of coal that can withstand the laser desorption process and be detected. The problem of disrupting the functional group to derivative bond can therefore be overcome by more careful selection of derivatizing agents, and by lowering the laser power density.

FUTURE WORK

Work will proceed with further use of FMP and TMS on highly oxidized coals, both using gas phase reactions and direct derivatization. DRIFTS will also be performed on reacted coals to monitor changes in hydroxy and carbonyl bands, indicative of derivatization.

REFERENCES

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FIG. 1

GAS PHASE REACTOR

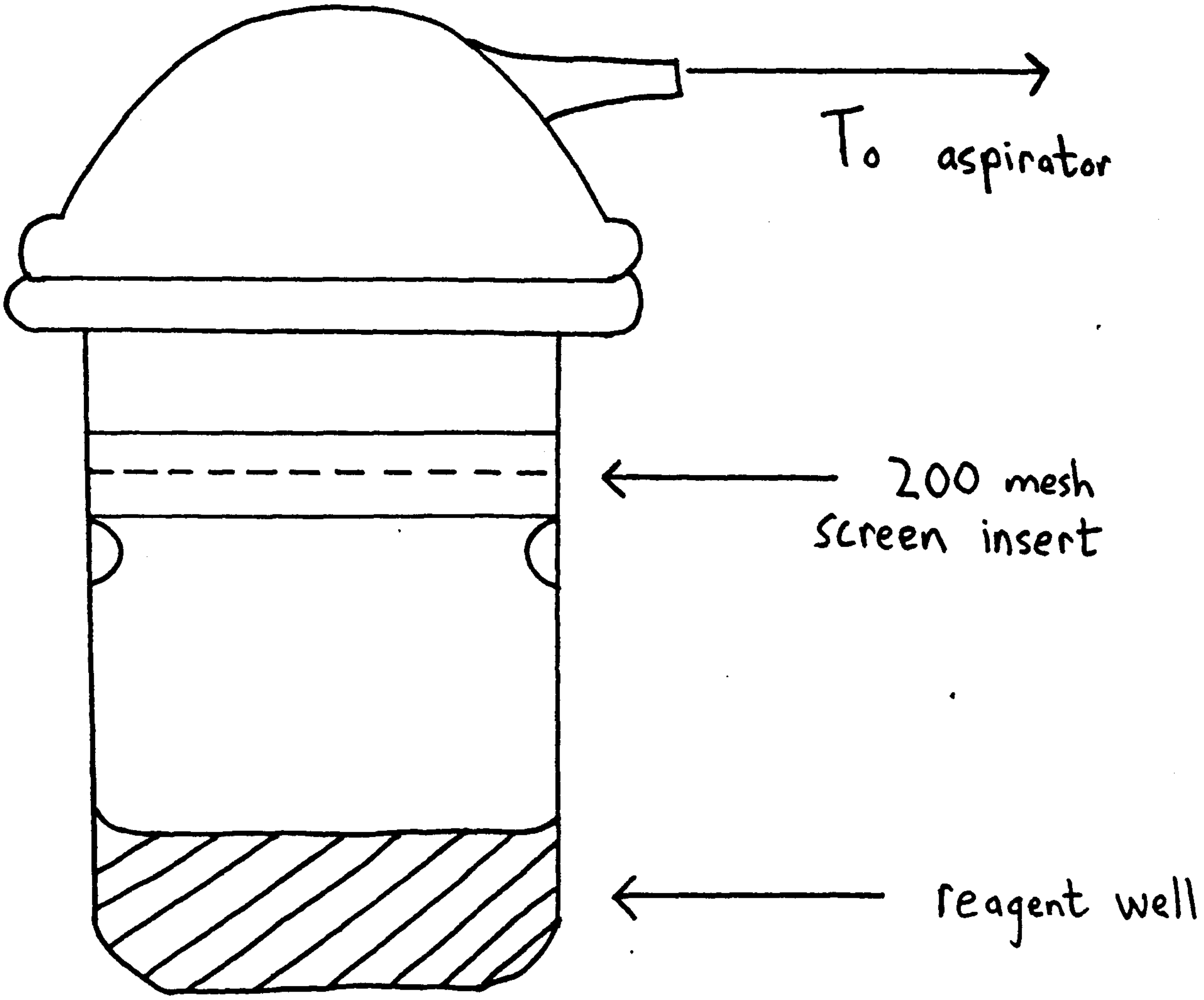


FIG. 2A

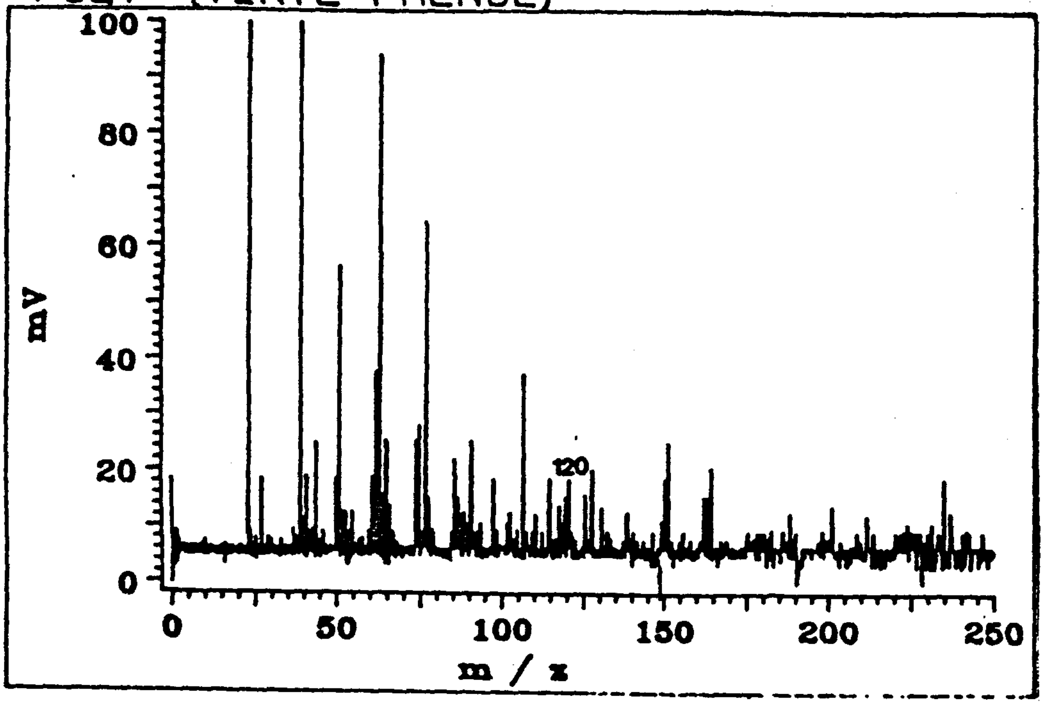
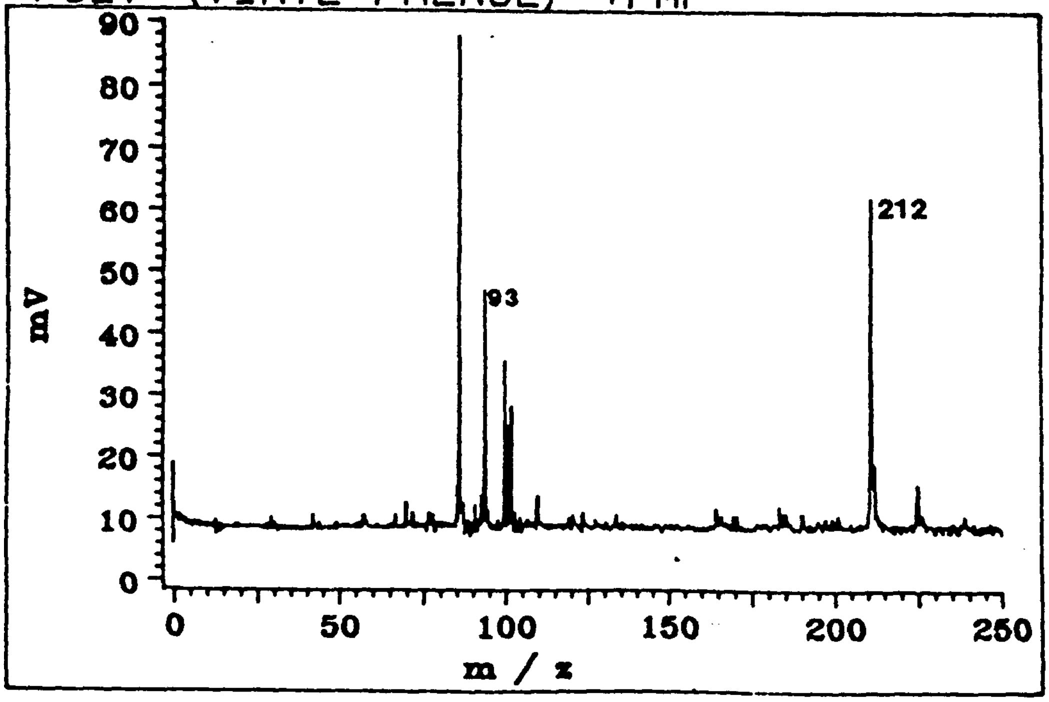
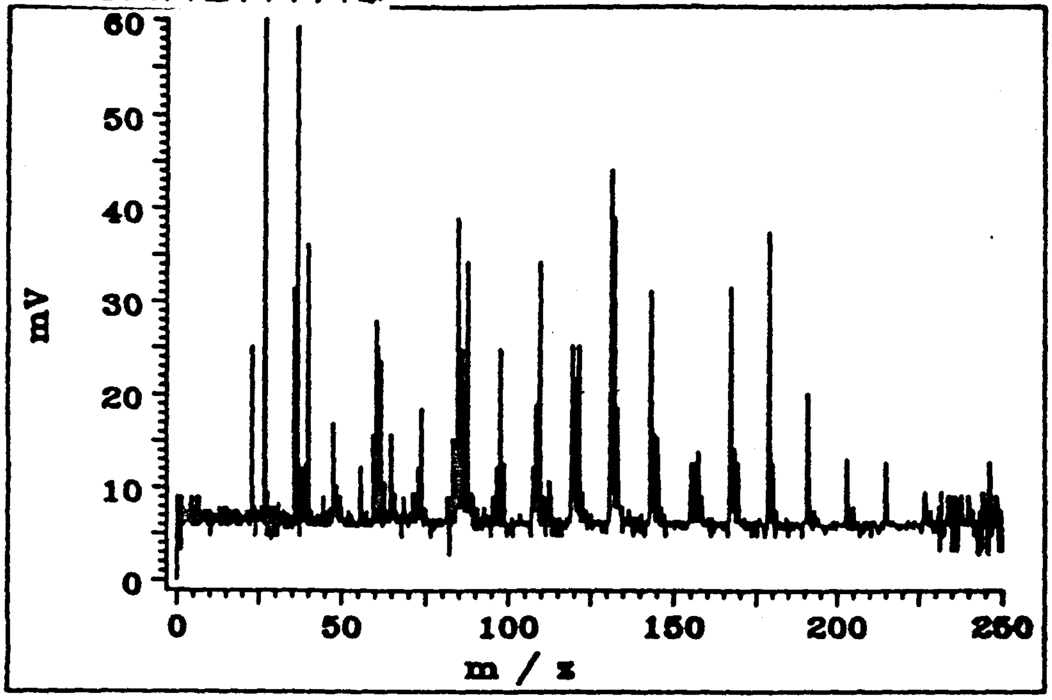

POLY (VINYL PHENOL)

FIG. 2B


POLY (VINYL PHENOL) +FMP

POCAHONTAS

FIG. 3A



POCAHONTAS + FMP

FIG. 3B

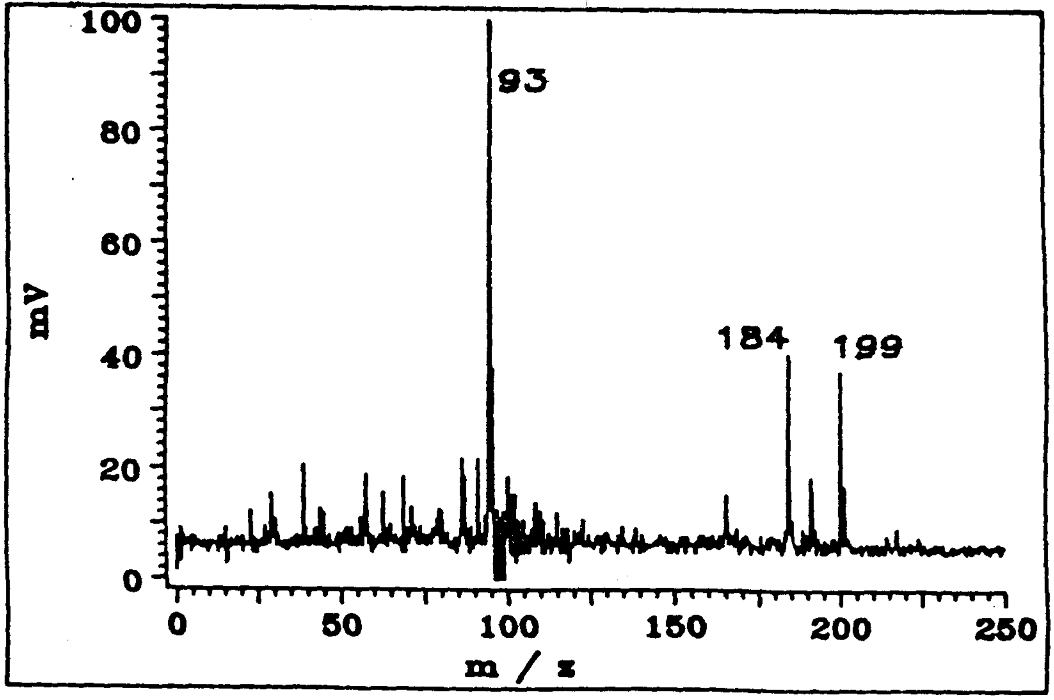
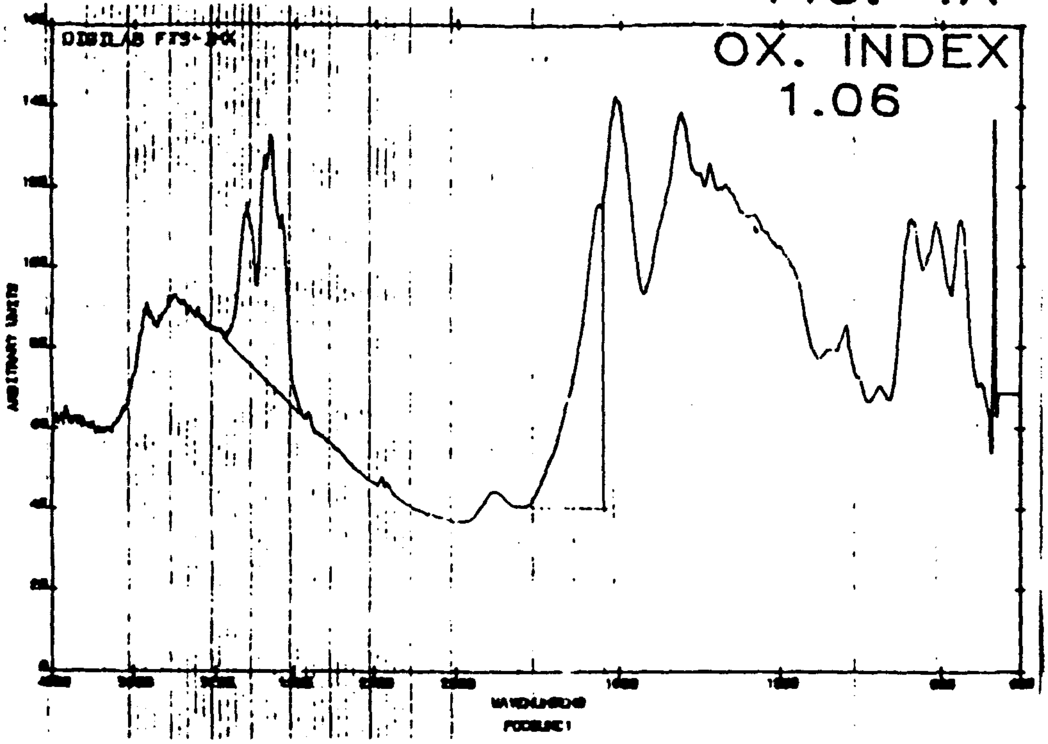


FIG. 4A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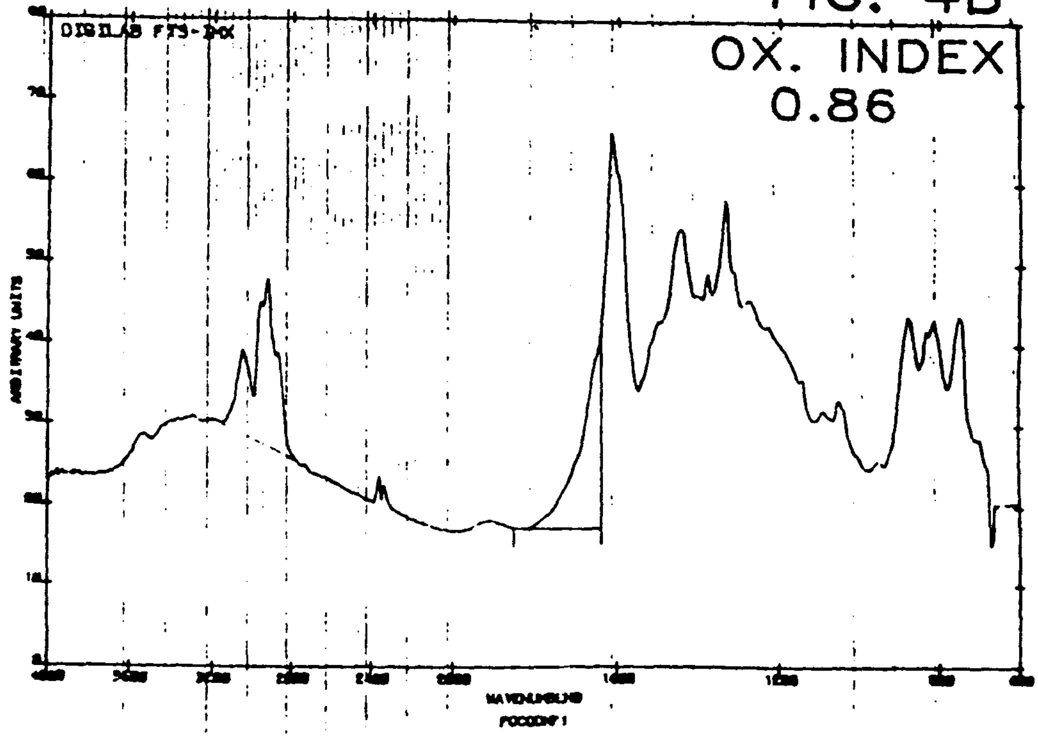
1.06
ARBITRARY UNITS
WAVENUMBERS

FIG. 4B


DIGILAB FTS-IMX
OX. INDEX
0.86
ARBITRARY UNITS
WAVENUMBERS

NAPHTHOL + TMS (GAS PHASE)

FIG. 5