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# CHARACTERIZATION OF COAL LIQUEFACTION PRODUCTS BY GAS CHROMATOGRAPHY–FOURIER TRANSFORM INFRARED SPECTROSCOPY–MASS SPECTROMETRY

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## SUMMARY

An integrated gas chromatography Fourier transform infrared spectroscopy–mass spectrometry system was utilized in the analysis of a neutral and acidic fraction obtained from the aqueous portion of the low-severity coal liquefaction products. Reconstructed selected-ion chromatograms along with reconstructed absorbance chromatograms over elected ranges were useful in discriminating between the types of organic compounds in the complex mixtures. A series of $\gamma$-lactones and a series of ketones were characterized, the ring size and unsaturation being determined by the absorbance frequency of the carbonyl stretching band.

## INTRODUCTION

The integration of capillary gas chromatography (GC) with both Fourier transform infrared spectroscopy (FT-IR) and mass spectrometry (MS) has resulted in a powerful method for the characterization of complex mixtures. The advantages of these linked GC–FT-IR–MS systems have been discussed by several authors[1–4]. The analysis of components separated on the high-resolution capillary column by both IR spectroscopic and MS techniques greatly increases the confidence in identification of the components of the mixture. MS and vapor-phase library search results can be compared to eliminate incorrect or false-positive library identifications. For compounds the spectra of which are not in the libraries, the identification by logical analysis of the two spectra is a tremendous advantage. Furthermore, by examining and comparing the reconstructed chromatograms of selected ions from the stored MS data and the FT-IR absorbance reconstructions over selected frequency ranges corresponding to absorptions of functional groups, the analyst can rapidly assess the compound classes of various components of the complex mixture.

This report describes the use of an integrated GC–FT-IR–MS system for the identification of the volatile components which result from the conversion of coal into liquid and gaseous fuels. Initially our focus has been on the water-soluble products obtained in low-temperature (low-severity) experiments with low-rank coals. The system, developed at the University of North Dakota Energy Research Center, for

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these analyses consists of a capillary gas chromatograph interfaced serially with the light pipe of an FT-IR spectrometer and an ion-trap detector[5]. The serial interface allows the total column effluent to pass through the FT-IR light pipe, thus maximizing the response from the less sensitive FT-IR instrument. Furthermore, the time scale is always the same for both FT-IR and ion-trap spectrometers, just shifted by a constant number of seconds. The amount of column effluent entering the mass spectrometer is readily adjusted by varying the make-up gas flow to the light pipe. Hydrogen carrier gas is used for better chromatographic performance. The FT-IR spectrometer is equipped with a coprocessor which rapidly transforms the interferograms and allows spectra to be stored on the disk along with part of the interferogram. Absorbance reconstruction of chromatograms can then be accomplished in a reasonable time from the stored spectra.

## EXPERIMENTAL

The GC–FT-IR–MS system was assembled with a Nicolet 20SXB FT-IR spectrometer and a Finnigan 700ITD, connected serially via an open-split interface, as described previously[5].

The low-severity coal liquefaction conditions and apparatus utilized for production of the products described in this paper will be described elsewhere. Prior to the GC–FT-IR–MS analysis, the organic products in the aqueous layer resulting from liquefaction of Beulah lignite at 325°C were first extracted into dichloromethane and then separated into a neutral and acidic fraction by extraction of the dichloromethane extract with sodium hydroxide solution. The acid fraction recovered by acidification of the base extract and extraction into dichloromethane was analyzed by on-column injection on the GC–FT-IR–MS system.

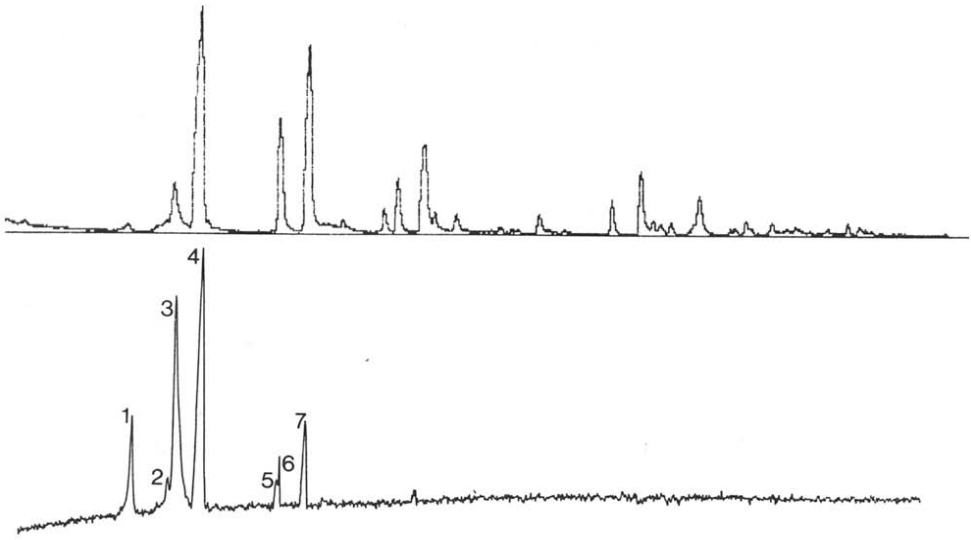


Fig. 1. Chromatograms of the acidic fraction: (top) total ion reconstruction; (bottom) Gram–Schmidt reconstruction. For peaks, see text.

## RESULTS AND DISCUSSION

The total ion reconstructed chromatogram and the Gram Schmidt (FT-IR) reconstructed chromatogram[6] of the acidic fraction from the low-severity products (Fig. 1) showed somewhat different responses to the components in the sample. The more intense peaks in the Gram–Schmidt reconstructed chromatogram were phenol and cresols (peaks 4, 5 and 7), which were present in high concentrations, and a series of lactones (peaks 1, 2, 3 and 6), which have not been previously identified in liquefaction products. Other phenolics present in lower concentrations appeared in the reconstructed ion chromatogram but not in the Gram-Schmidt reconstruction.

Characterization of the lactone series was aided by examining the absorbance-reconstructed chromatogram, which was obtained for the range 1800–1900 $cm^{-1}$ (Fig. 2). The absorbance maxima for all of the lactones were actually between 1808 and 1818 $cm^{-1}$, indicating that the lactones are $\gamma$-lactones. In this fraction, no carbonyl absorptions were found for the range 1700–1800 $cm^{-1}$, indicating that there were no $\delta$-lactones present, and that the ketones which were present in the neutral fraction (see discussion below) had not been extracted into the basic solution so as to contaminate the acidic fraction.

$\gamma$-Butyroactone and $\gamma$-valerolactone (peaks 1 and 3 in Fig. 2) were identified by matching FT-IR library spectra. The mass spctra of these components were identical

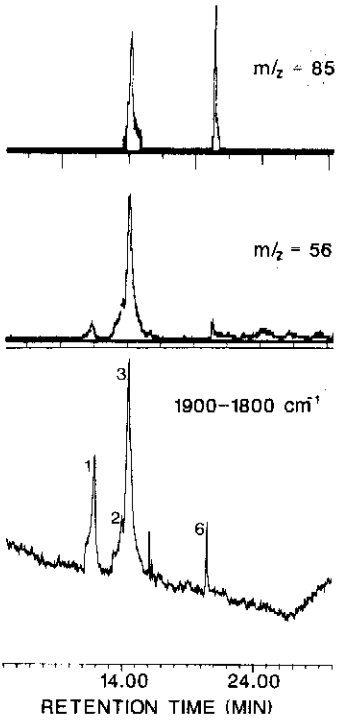


Fig. 2. Chromatograms of the acidic fraction: (top) $m/z$ 85 reconstruction; (middle) $m/z$ 56 reconstruction; (bottom) absorbance-reconstruction over 1800–1900 $cm^{-1}$. For peaks, see text.

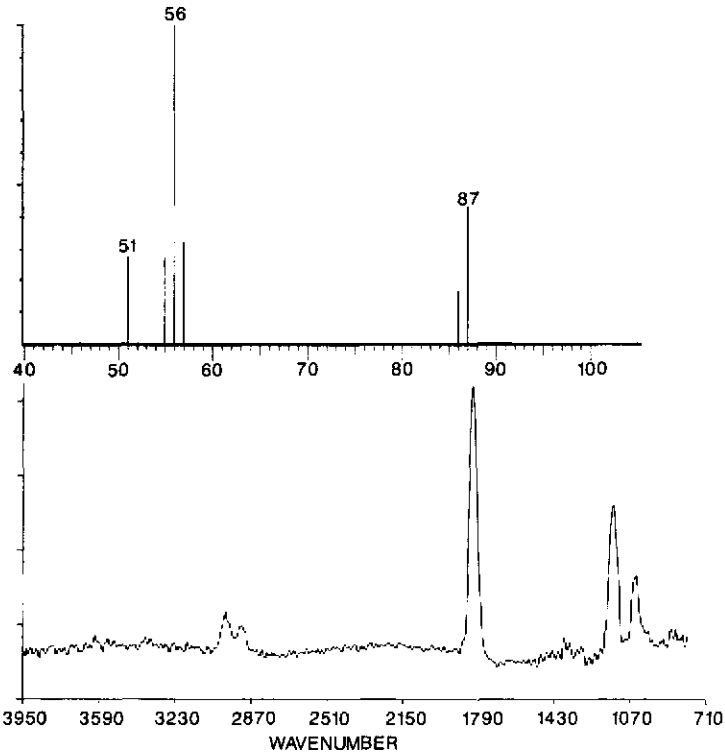


Fig. 3. Spectra for peak 1 in Fig. 2 ($\gamma$-butyrolactone): (top) mass spectrum (ion-trap detector); (bottom) FT-IR spectrum.

to library spectra, except that the ion-trap spectra of the butyrolactone (Fig. 3) and valerolactone exhibited $(M + 1)^+$ ions at *m/z* 87 and 101, respctively, in addition to the $M^+$ ions at *m/z* 86 and 100. The original commercial ion trap (Finnigan 700ITD) used in these studies was subject to self-chemical ionization (self-CI) effects for certain classes of compounds[5]. Because of the relatively high source pressure, certain oxygen-containing and other basic compounds were observed to undergo protonation and other adductive reactions with the large concentration of ions present during the storage cycle. Thus, esters and amines frequently exhibited the $(M + 1)^+$ ions in their spectra. The $(M + 1)^+$ ions were shown be narrow peaks, rather than the broad type of peak which can result from space-charging and saturation in the ion trap and whose masses are then incorrectly assigned by the data system. When the $M^+$ ion is absent from the spectrum, observation of the $(M + 1)^+$ ions can then give molecular weight information, as in CI-MS with reagent gases.

Fragmentations and self-CI protonation for $\gamma$-butyrolactone and $\gamma$-substituted lactones are shown in Figs. 4 and 5. The $\gamma$-alkyllactones characteristically lose the alkyl group to give the *m/z* 85 fragment ion. Loss of the $\gamma$-carbon with its attached atoms results in the *m/z* 56 cyclopropanone ion. Selected-ion reconstructions for *m/z* 85 and *m/z* 55 will discriminate the lactones on the basis of positional isomerism (or ring size. if

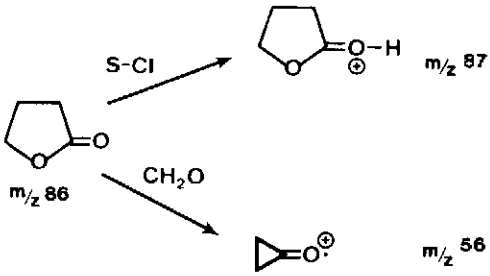


Fig. 4. Fragmentation of γ-butyrolactone.

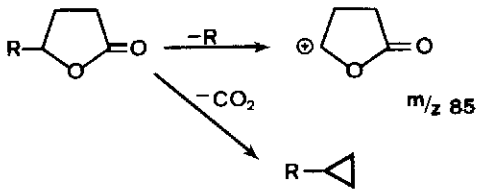


Fig. 5. Fragmentation of γ-alkyllactones.

other lactones were present). The *m/z* 85 and 56 reconstructions for the acidic coal liquefaction sample are shown in Fig. 2, along with the absorbance reconstruction.

Besides the butyrolactone and valerolactone, two other lactones were present in small amounts, peak 2, which lacked the *m/z* 85 ion, and peak 6, which exhibited the *m/z* 85 ion. The retention time and mass spectrum of peak 2 matched those of α-methyl-γ-butyrolactone. However, the β-methyl isomer cannot be ruled out, since the mass spectrum of this lactone would also lack the *m/z* 85 ion. The β-isomer or its library FT-IR spectrum or mass spctrum were not available for comparison. Peak 6, which was partially separated from *o*-cresol (peak 5) was identified as γ-ethyl-γ-butyrolactone because of the $(M + 1)^+$ ion at *m/z* 115, the large fragment ion at *m/z* 85 (base peak) which resulted from loss of γ-ethyl radical, and the lack of *m/z* 99 ion, characteristic of the dimethyl-substituted butyrolactones.

The phenolic components of the sample were easily identified by the mass spectra and the retention times. This aspect of the analysis was routine, and since only the usual phenolic products found in coal-derived liquors were identified, the results will not be discussed here. Except for phenol and cresols, the FT-IR spectra of the phenolics from this set of data were not usable due to a low signal-to-noise ratio. However, a more concentrated sample gave spectra which confirmed the phenol identification. Only trace levels of guaiacols and catechols were present in this sample.

Characterization of the neutral fraction by GC–FT-IR–MS showed that a large variety of polar organic components were present (Fig. 6). These components were identified as cyclic alcohols, cyclic ketones and unsaturated cyclic ketones. A trace of the phenolics and one of the lactones has carried over into this fraction as a result of incomplete extraction. This is a common problem in the analysis of aqueous coal-derived materials, which requires continual inspection. Absorbance-reconstructed chromatograms for the carbonyl region (1700–1800 $cm^{-1}$) and reconstructed chromatograms of *m/z* 55 fragment ions were highly selective for the cyclic ketones.

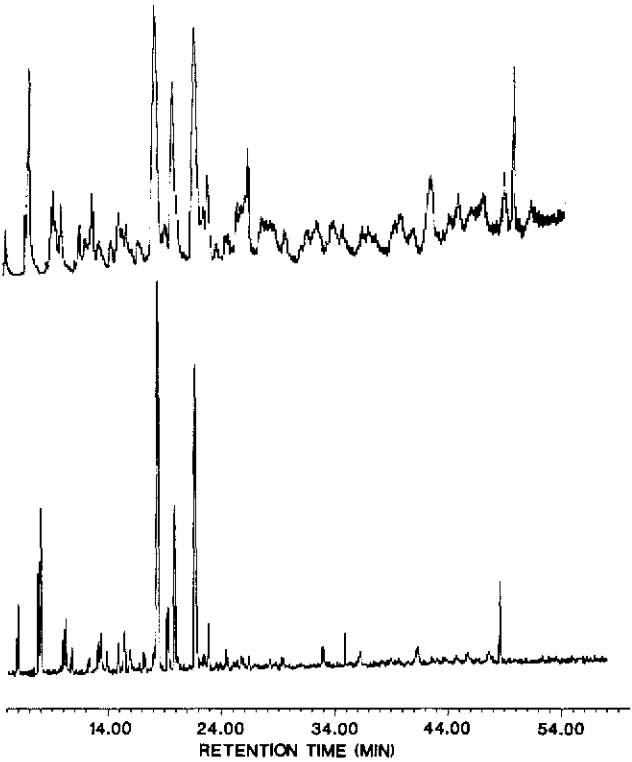


Fig. 6. Chromatograms of the neutral fraction: (top) total-ion reconstruction; (bottom) Gram–Schmidt reconstruction.

The unsaturated cyclic ketones were identified by the reconstructed chromatograms of *m/z* 53 ions and the carbonyl absorbance reconstruction. Reconstructed ion chromatograms of *m/z* 57 iobs and absorbance-reconstructed chromatograms for the hydroxyl stretching region identified the cyclic alcohols.

The first portions (12 min) of these reconstructed chromatograms are shown in Fig. 7. From the 1700–1800 $cm^{-1}$ absorbance reconstruction, peaks 2, 3, 5, 7, 8, 9, 10 and 11 were characterized as cyclic ketones. These characterizations were confirmed for peaks 2, 3, 5, 7, 8, 9 and 11 by examining the *m/z* 55 ion chromatogram and for peak 10 by examining the *m/z* 53 chromatogram. Each component was then identified from the individual IR and mass spectrum. IR spectra showed that peaks 2, 3 and 5 were cyclopentanones (1759 $cm^{-1}$) and that peak 10 was a cyclopentenone (1737 $cm^{-1}$) (Fig. 8). Thus peaks 2, 3 and 5 were cyclopentanone ($M^+$ at *m/z* 84), 2-methylcyclopentanone, and 3-methylcyclopentanone ($M^+$ at *m/z* 98). Mass and FT-IR spectra of these components matched library spectra. Peaks 7, 8, 9 and 11 were $C_2$-cyclopentanone isomers ($M^+$ at *m/z* 112), the structures of which could not be further elucidated because of lack of standards and library spectra. Peak 10, which was partially separated from the $C_2$-cyclopentanone, was identified as a methylcyclopentenone from the mass spectrum ($M^+$ at *m/z* 96). The mass spectrum from peak 10 (Fig. 8) did not match the U.S. Environmental Protection Agency/National Institutes

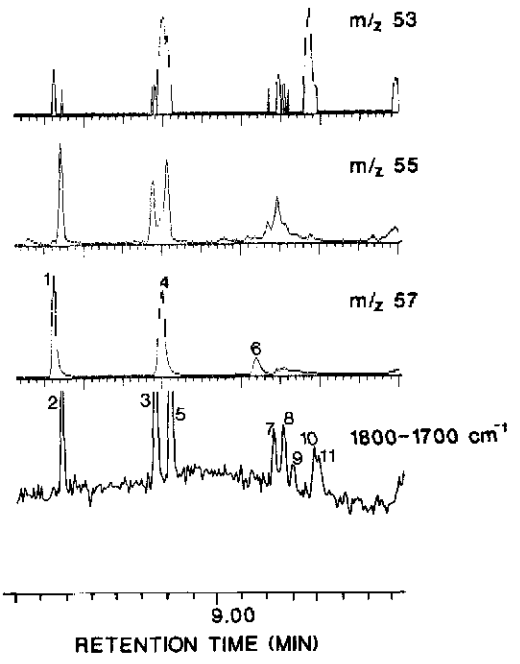


Fig. 7. Chromatograms of the neutral fraction: (top) *m/z* 56 reconstruction; (upper middle) *m/z* 55 reconstruction; (lower middle) *m/z* 57 reconstruction; (bottom) 1700–1800 $cm^{-1}$ absorbance reconstruction. For peaks, see text.

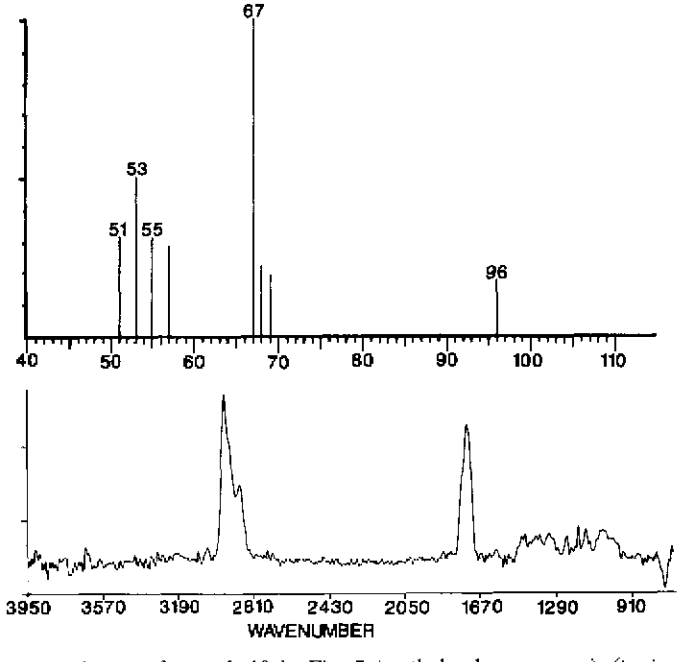


Fig. 8. Spectra for peak 10 in Fig. 7 (methylcyclopentanone): (top) mass spectrum; (bottom) FT-IR spectrum.

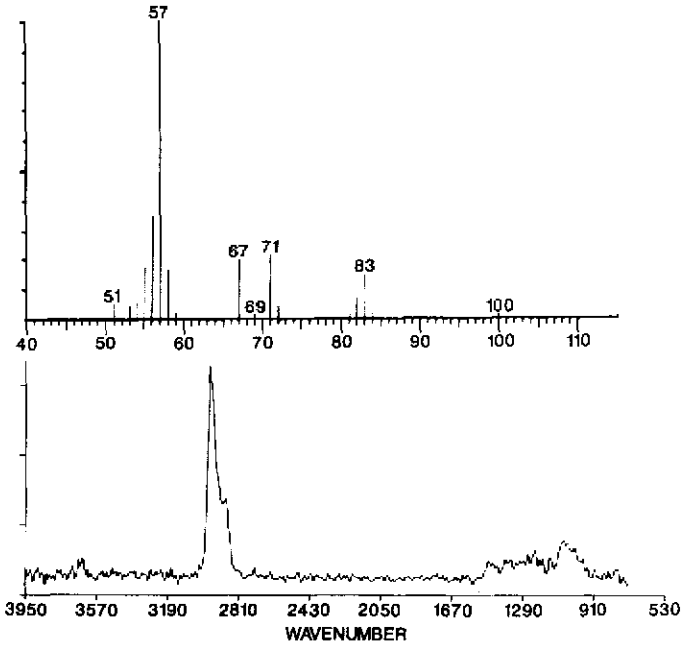


Fig. 9. Spectra for peak 4 in Fig. 7 (2-methylcyclopentanol): (top) mass spectrum; (bottom) FT-IR spectrum.

of Health library spectra of 2-methyl- or 3-methylcyclopentenone. More highly substituted alkyl-cyclopentenones and indanones were eluted later in the chromatography of this sample.

The alcohols in the sample were distinguished by the *m/z* 57 reconstructed-ion chromatogram (peaks 1, 4 and 6 in Fig. 7). The IR spectra of these peaks exhibit the hydroxyl-stretching absorption at 3650 $cm^{-1}$, which is characteristic of alcohols, and none have the carbonyl absorption, which clearly establishes that none are lactones or ketones. The IR spectrum of Peak 4 is shown in Fig. 9 as an example. The three alcohol components (peaks 1, 4 and 6) were identified as cyclopentanol, 2-methylcyclopentanol, and cyclohexanol by matching library FT:IR and mass spectra. The mass spctra of the three alcohols show very weak or no molecular ions and small $(M - 17)^+$ or $(M - 18)^+$ ions. For example, the mass spectrum of peak 6 had an ion at *m/z* 82 but no molecular ion at *m/z* 100. The characterization of these alcohols was aided considerably by having both IR and MS data on each component peak. No alcohols larger than cyclohexanol were present in the sample.

Many of the components of the liquefaction samples either were compounds whose spectra were not in the library or were isomers having similar spectra. Examination of both the MS and FT-IR spectra aided in the identification. Improvements in the analysis will result from greater FT-IR sensitivity, which will improve the spectra of the smaller peaks and allow us to utilize more of the weak but highly diagnostic IR bands in the identification.

ACKNOWLEDGEMENTS

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