Quarterly Report 6/1/92

TITLE: Novel Technique for Coal Pyrolysis and Hydrogenation Product Analysis

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OBJECTIVE: The overall objective of this study is to establish vacuum ultraviolet photoionization-MS and VUV pulsed EI-MS as useful tools for a simpler and more accurate direct mass spectrometric measurement of a broad range of hydrocarbon compounds in complex mixtures for ultimate application to the study of the kinetics of coal hydrogenation and pyrolysis processes. The VUV-MS technique allows ionization of a broad range of species with minimal fragmentation. Many compounds of interest can be detected with the initial wavelength used (118 nm), but additional compound selectivity is achievable by tuning the wavelength of the photo-ionization source in the VUV. Other techniques for discrimination of molecular isomers such as series mass filters and metastable ion decay experiments have also been investigated as means to achieve compound selectivity.

WORK DONE AND CONCLUSIONS: This report covers the last quarter of the last year of the three-year grant period. In the final project year, we concentrated on the pyrolysis and oxidative pyrolysis of large hydrocarbons and mixtures of large and small hydrocarbons in order to develop the VUV-MS technique for compounds more representative of those in coal pyrolysis applications. Special focus was directed at the pyrolysis and oxidative pyrolysis of benzene and benzene acetylene mixtures. The acetylene/benzene mixtures were used to gain a better understanding of the mechanisms of molecular growth in such systems specifically to look at the kinetics of aryl-aryl reactions as opposed to small molecule addition to phenyl radicals. Sarofim and coworkers at MIT have recently demonstrated the importance of these reactions in coal processing environments. In the past, the growth mechanism for the formation of mid-sized PAH has been postulated to involve primarily successive acetylene additions to phenyl-type radicals, our work confirms this as an important mechanism especially for smaller PAH but also investigates conditions where biaryl formation can play an important role in higher hydrocarbon formation.

In the first two quarters of the current project year, we carried out the pyrolysis of mixtures of these compounds without oxygen in a microflow reactor. In the current report period experiments were repeated in the presence of various amounts of oxygen and for low conversion oxidation conditions. Two different temperature regimes are considered: below 1000 K, where reactivity is dominated by molecular processes, and above 1100 K, where radical chain mechanisms become the dominant fuel consumption pathway. These experiments were carried out over a 1.5 order of magnitude range of

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total pressures and with different diluents. Figure 1 shows mass spectra for the oxidative pyrolysis of benzene at 350Torr in an Ar diluent at a fuel air equivalence ratio of 0.79. Note that phenol is the first product detected as temperature is increased and that some mass 128 was detected even at very low benzene conversions. Benzene conversion for all runs shown was less than 10%, and the benzene peak is off scale on all traces shown. This data agrees well with the product spectra observed for similar reaction conditions by Glassmann and coworkers in their fast-flow reactor. This is an important observation in checking the applicability of our microreactor geometry for hydrocarbon kinetics experiments.

A quadrupole mass analyzer with electron ionization was set up in the ionization chamber of the VUV-MS to allow the analysis of molecular species whose ionization potentials are above our present VUV capabilities and to provide another measurement to quantify the VUV-MS data.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This research is innovative, offering a relatively new technique with significantly improved performance for the mass detection of $> C_1$ hydrocarbons in mixtures. This technique would facilitate the scientific investigation of coal upgrading processes such as pyrolysis and hydrogenation by allowing accurate direct analysis of both stable and intermediate reaction products. The on-line, non-destructive nature of the VUV-MS technique facilitates data collection and analysis, allowing more experiments to be run with greater analysis accuracy, greatly improving the database and allowing more confident prediction of reaction pathways.

PLANS FOR THE COMING PERIOD: Since this is the end of a 3 year grant period on development of a diagnostic instrument we are now focusing on designing improvements to the technique to make it a more general tool capable of isomeric discrimination.

The principle benefit of VUV ionization using non-resonant, low intensity laser beams is the relatively soft ionization which it provides. While molecular ion identification is greatly simplified, successfully analyzing the structure of the species is not possible because of the multiple structures at a single mass which are not selectively ionized. Using both VUV radiation and laser generated electron ionization, structural information can be obtained but only in a system with a small number of components where dissociative relationships between parent and daughter ions are characterizable. This is clearly not the case when conducting high temperature pyrolyses of hydrocarbons, in which a large sample of various molecular weight ions are simultaneously present. Moreover, many of these species, if fragmented in some dissociative process, will decompose into mass channels already occupied, further obscuring the data without performing computationally intensive deconvolution.

It would therefore be of significant benefit if the mass analyses of the VUV produced ions could be modified to yield structural information. One alternative to achieve this would be to include separate and independent devices for parent ion selection, dissociation of the chosen parent (either actively or by metastable ion decay) and subsequent mass analysis of the daughter ions for a confirming structural analysis. The requirements of the first mass filter would be controllability of the selected mass-to-charge range which is selected to pass, as well as high transmission (ca. 90% or more) throughout this range. Only tandem instruments which incorporate Time of Flight as the second mass filter will maximize sensitivity, since the dispersion of daughter ions is longitudinal and not lateral. This allows a much greater number of ions of all possible masses to reach the detector, rather than just ions of a single mass which satisfy the temporal scanning function of some electric or magnetic field.

A general schematic of the proposed instrument optimized for VUV photoionization is shown in Fig. 2. Incorporating the aforementioned suggested improvements for greater sensitivity, equal or greater mass resolution and ability to distinguish isomeric components, it consists of the standard laser based VUV photoionization method and a time-of-flight mass filter, separated by a two sector ($E \times B$) mass spectrometer and a dissociation cell. In practice, this device could be run manually and, in the absence of a dissociation media, set to transmit molecules of all mass-to-charge values simultaneously for complete parent ion data, much as a single TOF instrument is used. Alternately, the window of mass-to-charge values accepted by the electric-magnetic sector combination could be narrowed to a very finite (i.e. single value) range, allowing the user to then adjust the dissociation conditions for some most informative fragment ions to be produced. Data treatment would be through either pulse counting or analog circuitry, depending on signal amplitudes and repetitiveness.

In summary, the utility of a VUV photoionization-MS technique for the analysis of multi-component hydrocarbon species in complex mixtures would be optimized with the following instrument improvements.

1. Better matching of the neutral-producing and photon-producing duty cycles and use of ion counting techniques to improve detection sensitivity.
2. Tunable ionization wavelength, tandem mass filters and/or the study of dissociation of the parent ions to obtain structural discrimination at a given mass.

HIGHLIGHT ACCOMPLISHMENTS

1. The extension of previous hydrocarbon system work to systems where hydrocarbons containing oxygen are detected.
2. Confirmation of benzene oxidation kinetics including semiquantitative measurement of cyclohexadienyl radical concentration. Complete analysis of this system will be presented in the project's final report.
3. Development of correlations for VUV photoionization yields based on PES data is continuing. This work will be summarized in the final report as a means for obtaining semi-quantitative detection of hydrocarbon radicals without direct calibration of each species.

ARTICLES AND PRESENTATIONS

Pfefferle, L.D. "Higher Hydrocarbon Growth During Benzene Pyrolysis" abstract for 1992 Annual AIChE Meeting, Miami, Fl. 11/92.

The PhD Thesis "The Detection of Soot Precursors from a Microjet Reactor Using Vacuum Ultraviolet Photoionization Mass Spectrometry" of the graduate student has been drafted and will be defended in 1/93.

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Figure 1. Product Spectra During the Oxidation of Benzene at Increasing Temperature from 885-995 K and 20 ms Residence Time

Figure #2: Schematic of VUV ionization TOF-MS with mass filters to allow identification of mass isomers

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