Pyrolysis Analysis by Molecular Beam Mass Spectrometer

Extrel CMS, LLC
Application Note
Pyrolysis Analysis
RAP104A

The analysis of pyrolytic products is of great importance in today's chemical world. From biofuel analysis to understanding how jet fuels work, pyrolysis gives researchers a better grasp of what chemistry is taking place. However, pyrolysis is not without its hurdles. Highly reactive species, necessity for high throughput, and the presence of damaging particulates are some of the issues researchers face when using pyrolysis. The Extrel® VeraSpec™ MB family of molecular beam mass spectrometers (MBMS) seeks to knock down these barriers and provide researchers with a fast, accurate, and reliable instrument that can replace the older, slower analytical methods and techniques.

Challenges of Pyrolysis Analysis

- Highly Reactive Species
- Damaging Particulates
- Dirty Samples
- Cleaning Downtime
- Dead Time Between Sample Runs

Pyrolysis, Highly Reactive Species, & Discovery

One of the hot beds of pyrolysis research is fuel analysis. Two branches, jet fuels and biofuels, embody the challenges associated with pyrolysis. To understand thermally-stressed fuels, a robust understanding of chemical dynamics in hydrocarbons at elevated temperatures must be developed. Currently, there is a fundamental disconnect between the pyrolysis models developed from long dwell time studies and what is observed under molecular beam conditions. Thermally-stressed fuels form pyrolytic deposits. Researchers need to be able to predict and control these deposits. The current understanding of hydrocarbon pyrolysis comes from a wealth of gas-phase studies.[1,2] However, when jet engines are in operation, their fuel acts as a supercritical fluid. Few supercritical studies have been performed. Typically, researchers have had to infer the conditions experienced at elevated temperature and pressure by examining the state of the "fuel" before and after thermal stressing. This is because direct observation of the chemical processes, occurring under real-world pyrolytic conditions, has proven

PYROLYSIS & COMBUSTION

exceedingly difficult. Researchers currently search for a good understanding of the relationship between fuel composition and fuel performance. The Extrel VeraSpec MB systems can be used to probe the in-situ chemical dynamics in hot super-critical and gas-phase hydrocarbons. The ability to identify, by direct observation rather than inference, the key species along the reaction coordinate can be used to generate a “roadmap” for thinking about how these chemical systems differ from those that are already widely understood. This “roadmap” could aid in formulating corrections to kinetics data and mechanisms used to model fuel pyrolysis.

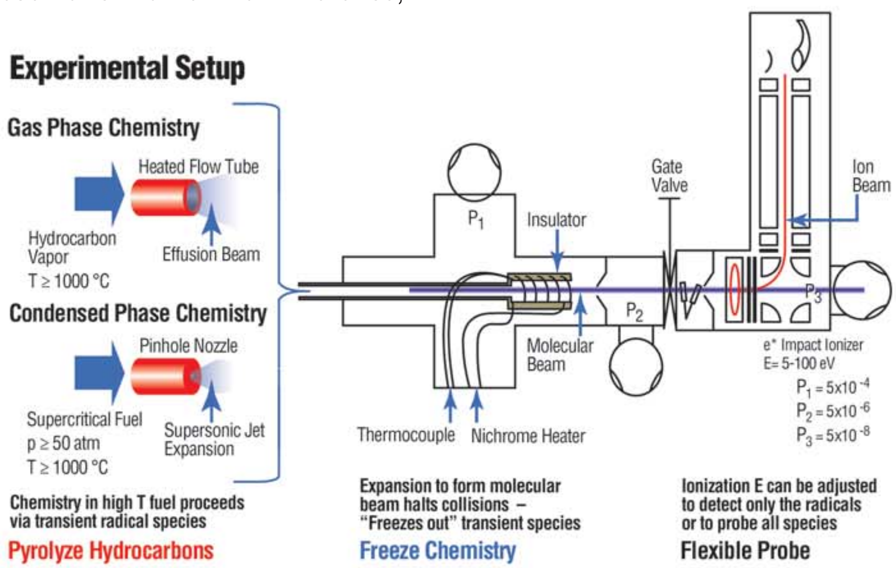

Figure 1.
Scheme of a pyrolyzer and MBx MS system used for real-time detection of pyrolytic products.

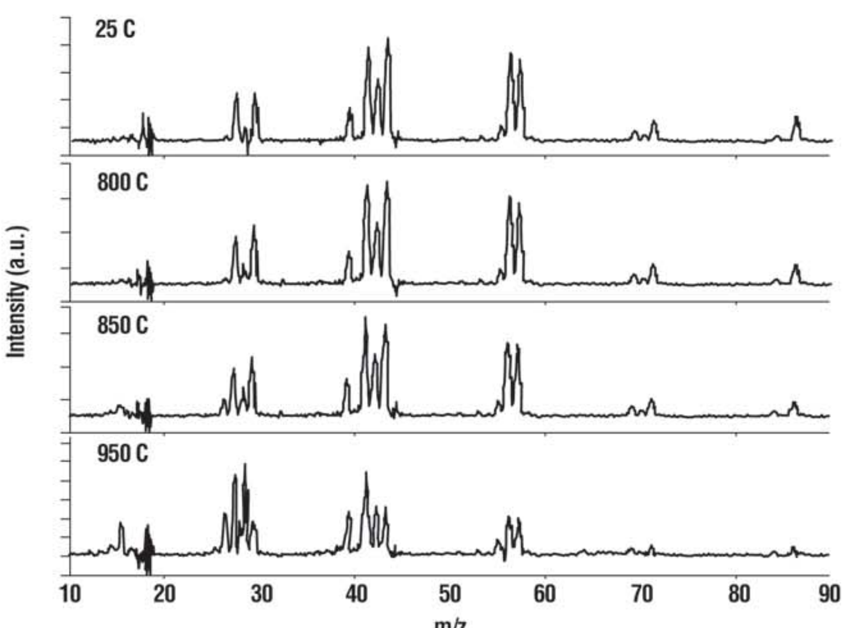

Figure 2.
Pyrolysis of Hexane versus Temperature.
Note the increased intensity of C1-C3 and the decreasing intensity of C4-C6 in the higher temperature runs.

Once the spectrum was collected, the unpyrolyzed spectrum of n-hexane was subtracted from the pyrolysis spectra. This was performed in order to look at the true trend of the data. Figure 3 shows that as temperature increases, a point is reached where the small, C1-C3, compounds appear and then their intensity increases exponentially.

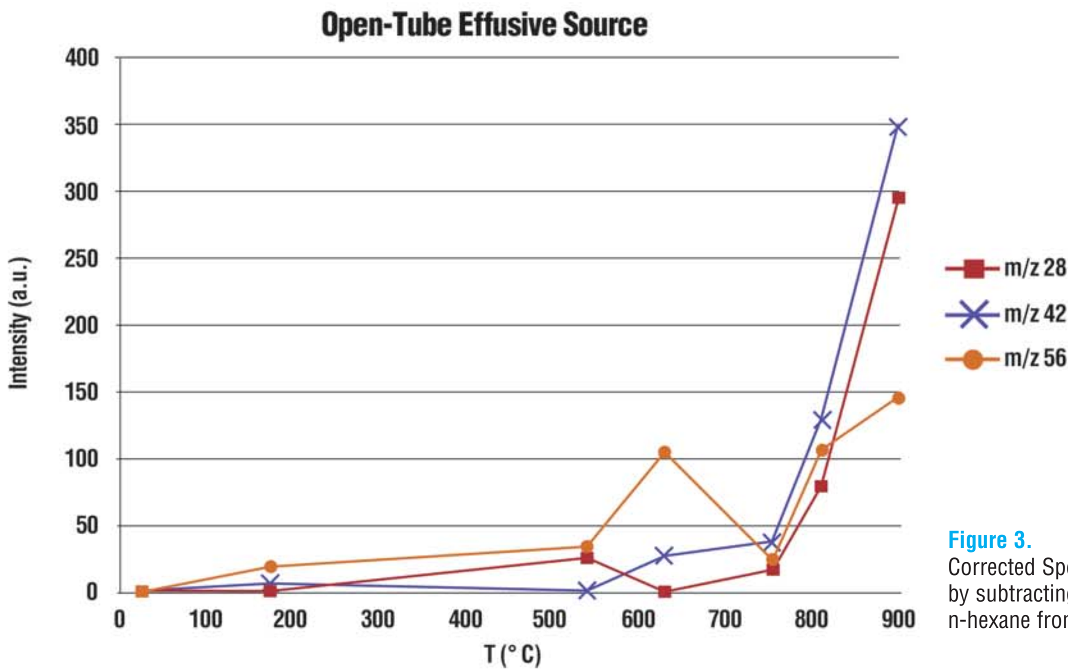

Figure 3.
Corrected Spectrum of pyrolysis products obtained by subtracting the Spectrum of Unpyrolyzed n-hexane from the Pyrolysis Spectrum.

When comparing the Pyrolysis/Molecular Beam mass spectrometry (Py/MBMS) data to the older analytical methodology data, the long residence times of the gas chromatograph (GC), in this case over an hour, compared to the millisecond time scale of the Py/MBMS causes a shift in the distribution of the n-hexane compounds. This is seen in the differences between the literature values in Figure 4 and the measured values seen in Figure 5.

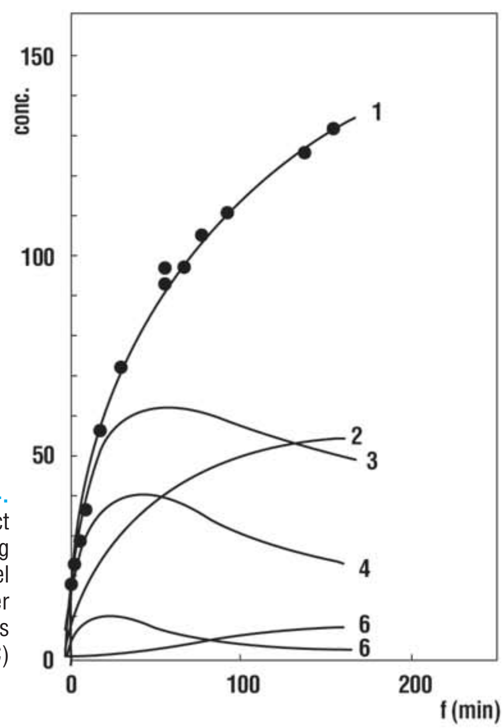

Figure 4.
Hydrocarbon product distribution with long reaction times. The label correlates with the number of carbons in the pyrolysis product. (200 min & 810 C)

Extrel
Core Mass Spectrometers

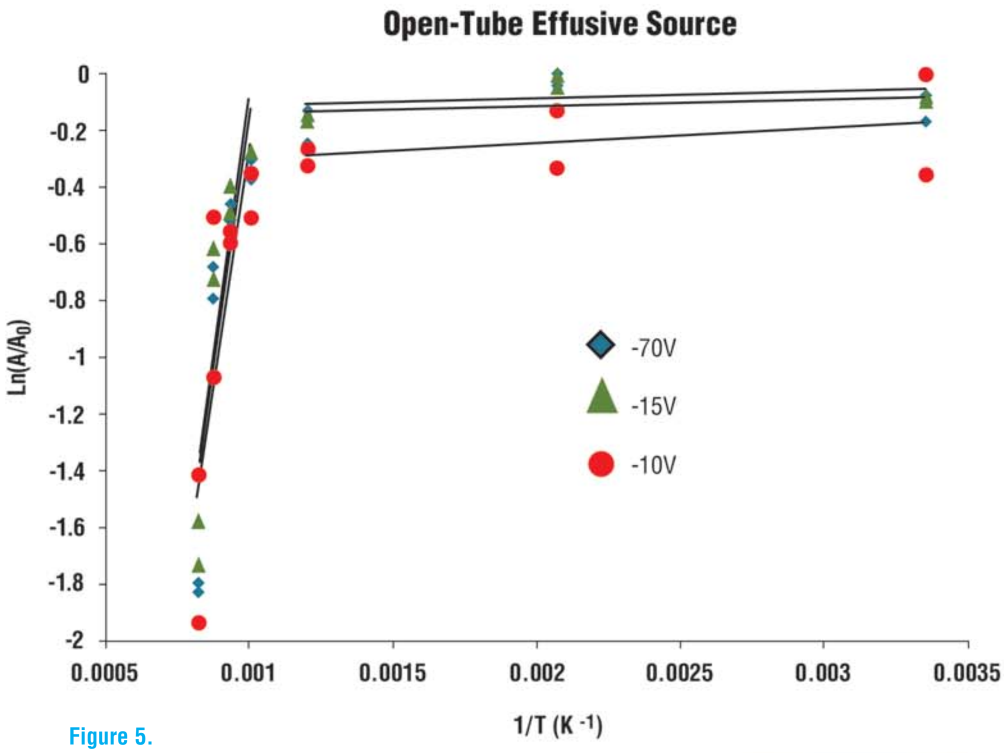

Figure 5.
Kinetic Plot of the Pyrolysis of n-hexane.

A kinetic study, seen in Figure 6, shows that the rate of disappearance of the M+ ion is independent of ionization energy - meaning that the pyrolysis of the hexane neutral is being measured, not the thermal fragmentation of the ion. Knowledge that the thermal fragmention is not being measured allows for the variance of ionization energy to be used to further explore the pyrolysis. This flexibility of measurement allows a researcher to make solid, confident, and accurate statements about their data.

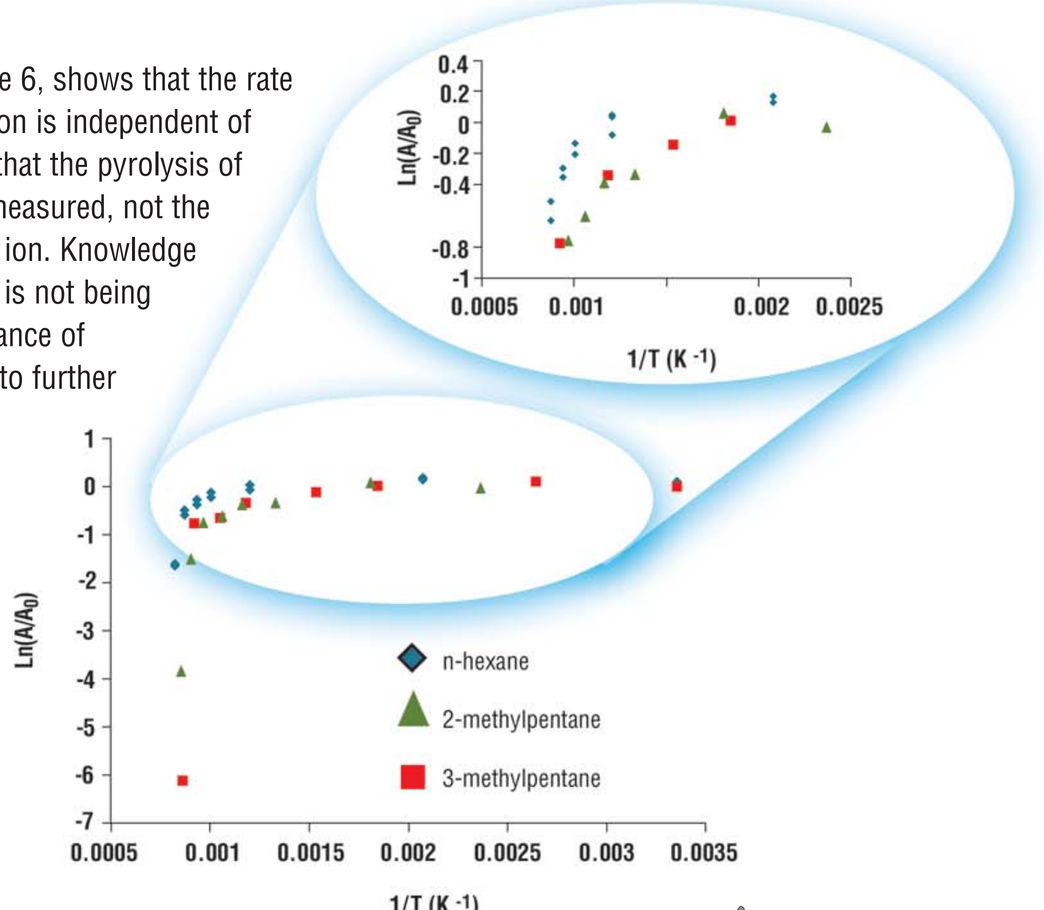

Figure 6.
Hexane Isomers as a Function of the Rate of Pyrolysis.

Particulates, Dead Time, & Dirty Samples

Aside from the gains the Extrel MB systems give to the analysis of highly reactive species, there are several other barriers to fast pyrolysis analysis. With the search for cleaner energy sources and the reduction of fossil fuel usage driving the energy industry today, analysis has developed into a multi-billion dollar industry. In any industry, time spent on samples, time between sample runs, and downtime for preventative maintenance and cleaning can slow down productivity and increase costs. In order to minimize these hurdles, Extrel worked with the National Renewable Energy Laboratory (NREL) to develop the VeraSpec MBx Molecular Beam Mass Spectrometer. The VeraSpec MBx features a custom-designed skimmer optical system that minimizes the presence of particulates and tar in the high vacuum chamber part of the system. This means that the mass spectrometer probe will accumulate virtually no particulates over time. When the skimmer system needs to be cleaned, the VeraSpec MBx's gate valve system allows for the mass spectrometer chamber to be isolated from the skimmer chamber. This allows the user to keep the system under vacuum for most preventative maintenance and cleaning operations. Since the mass spectrometer is not vented, downtime is reduced to hours, unlike a system that needs to be cooled, vented, and pumped back down to operating pressures, which can take a day or more.

"In four minutes, you can look at the spectrum … Prior to this (it) would take two people two weeks."

Figure 7.
The Extrel VeraSpec MBx features a custom skimmer optical system and gate valve to minimize instrument downtime due to cleaning.

The Extrel VeraSpec MBx tackles the analysis of problematic and dirty compounds that come out of the pyrolyzer without a need for chromatography or other separation techniques. This allows for true real-time analysis of the products versus the time-delayed analysis found when performing older, more traditional analytical techniques such as GC/MS. This ability was one of the reasons the VeraSpec MBx was chosen for the NREL's High-Throughput Analytical Pyrolysis (HTAP) system. The VeraSpec MBx enables the HTAP to thoroughly analyze hundreds of biomass samples a day, in an effort to determine the plant genotypes that are the most attractive for development of biofuels. Analysis of tree trunk core samples, that previously took two weeks, can now be done in minutes. That type of timesaving and real-time data production can potentially change the biomass industry. Mark Davis, the principal investigator behind the HTAP project, speaking about the real-time analysis the MBx provides, stated, "In four minutes, you can look at the spectrum and see that this sample reduces lignin by half… That's information, that prior to this, would take two people two weeks to acquire."

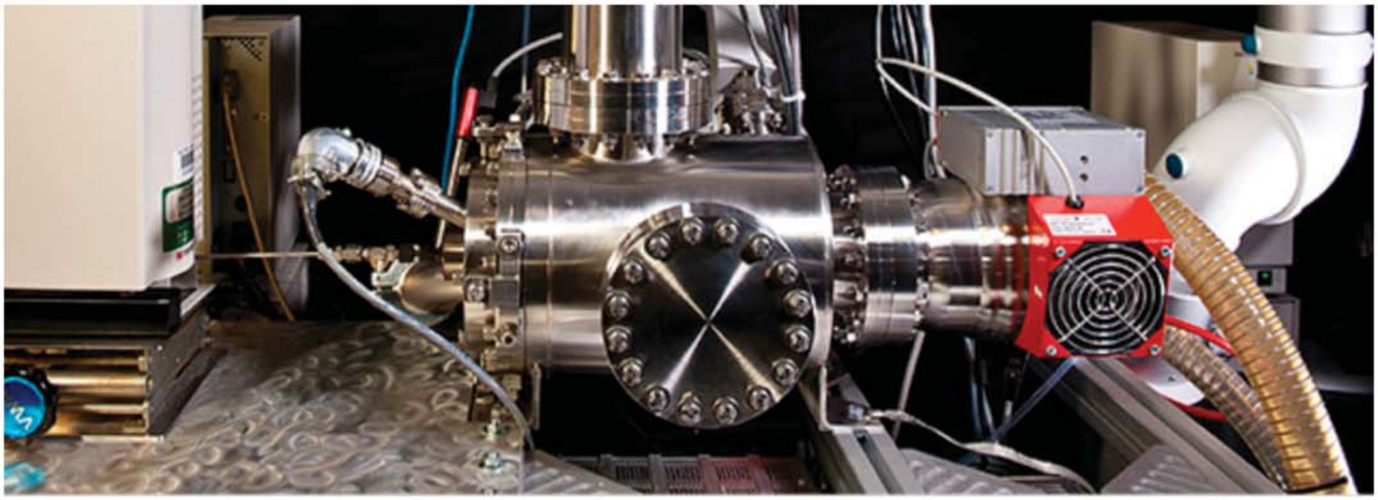

Figure 8.
The NREL HTAP system is built around the Extrel mass spectrometer.

The ability to analyze pyrolysis samples over a wide temperature range allows the researcher to view the components of their solid sample in a fast and accurate way. Figure 9a-c shows the variance among pyrolytic products from a sample of hot gas at varying temperatures. The data demonstrates the ability to see the full range of pyrolytic products, including the sensitivity to see the low intensity products across the mass range.

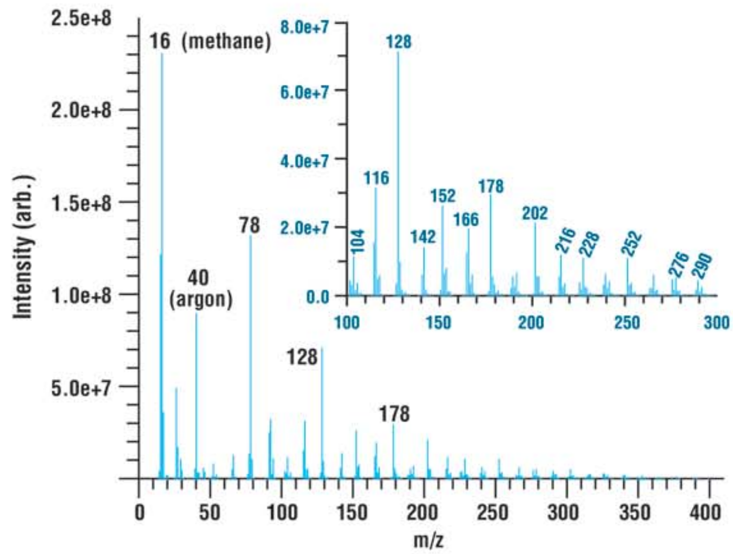

Figure 9a. Hot Gas py/MBMS spectra at 875 C.

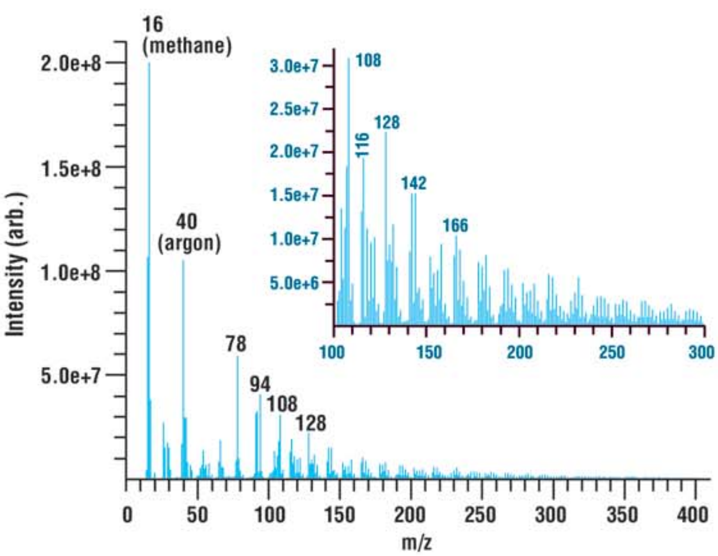

Figure 9b. Hot Gas Py/MBMS spectra at 750 C.

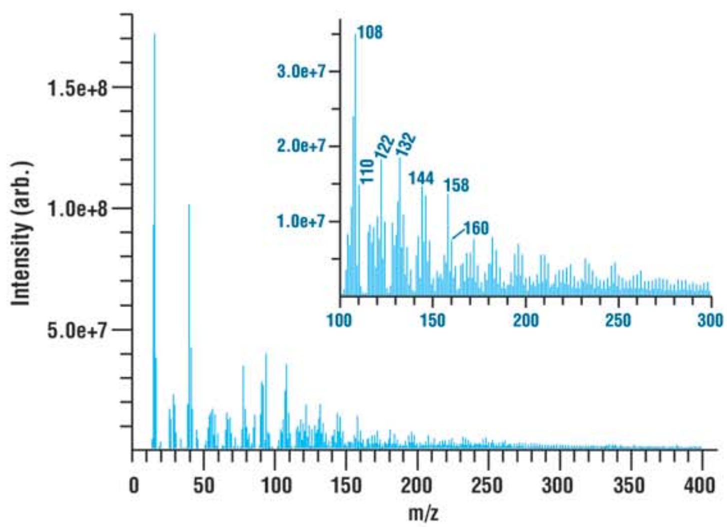

Figure 9c. Hot Gas Py/MBMS spectra at 650 C.

Extrel
Core Mass Spectrometers

A Solution to the Hurdles of Pyrolysis

Pyrolysis is a powerful analytical technique, however, it is not without its challenges. Highly reactive species, dirty samples, dangerous particulates, and complex spectra are all issues a researcher may run into when performing experiments.

The Extrel VeraSpec MB family of mass spectrometers takes advantage of the strengths of molecular beam science to overcome the issues normally prevalent with pyrolysis analysis. The design features of the MB family of mass spectrometers such as fast analysis to detect highly reactive species in real-time, the specially-engineered skimmer optics and gate valve minimizing downtime for cleaning, and the proven sensitivity, accuracy, and precision of the MAX probe, provide an accurate, stable, and flexible answer to the problems that accompany pyrolysis analysis.

The data that the MB family of systems collects is sensitive and selective enough for the measurement of highly-reactive intermediates in fuel analysis and is robust enough to allow for the detailed comparison of hundreds of samples a day for biofuel analysis. The Extrel VeraSpec family of Molecular Beam mass spectrometers, built on the proven strength of the MAX probe, is the ultimate solution for pyrolysis analysis.

Challenges and Solutions

Highly Reactive Species – Molecular Beam Science allows for real-time analysis.

Damaging Particulates and Dirty Samples – Skimmer Optical system to remove particulates.

Cleaning Downtime – The Gate Valve allows for the MS chamber to stay under vacuum.

Dead Time Between Sample Runs – The immediate measurement of pyrolysis by direct coupling to MS.

Acknowledgements

Mark Davis, Robert Sykes, and Danny Carpenter of NRELNathaniel L. Sanders and William K. Lewis from UDRI and WPAFB. Some data and figures were adapted from Sanders et al. ASMS 2012, Case Number: 88ABW-2012-2862

References

1 Corporan, E.; Edwards, T.; Shafer, L.; DeWitt, M.; Klingshirn, C.; Zabarnick, S.; West, Z.; Striebich, R.; Graham, J.; Klein, J. Energy & Fuels, 2011, 25, 955.

2 DeWitt, M. J.; Edwards, T.; Shafer, L.; Brooks, D.; Striebich, R.; Bagely, S. P; Wornat, M. J. in press at Energy & Fuels.

3 Ebert, K.H.; Ederer, H.J.; Isbarn, G. The Thermal Decomposition of n-Hexane Int. J. Chem. Kinetics 15, 475-502 (1983).

4 "Biomass Analysis Tool Is Faster, More Precise" NREL News Feature 2/26/2013 Bill Scanlon.

Extrel CMS maintains sales and service offices around the world.
Please contact us for the office nearest you or visit our website at **www.extrel.com**

Core Mass Spectrometers
www.extrel.com

Extrel CMS, LLC
575 Epsilon Drive – Suite 2
Pittsburgh, PA 15238-2838 USA
TEL: 412-963-7530 • FAX: 412-963-6578

QUALITY SYSTEM CERTIFICATION ISO 9001:2008
QUALITY MANAGEMENT SYSTEM
CERTIFIED BY DNV
ISO 9001:2008