DEFORMULATION AND COMPARISON ANALYSIS OF COALS USING MULTIPLE MODES OF PYROLYSIS-GC/MS

In the history of humankind, coal has always played a significant role in generating heat, cooking food, and even writing. Coal, a nonrenewable resource, is one of the most abundant fossil fuels. Formed million years ago, it also contains oil and gas. In general, there are three types of coals composed of different percentages of organic matters. Analyzing the chemical composition and distinguishing the different types of coals are major analytical protocols in the oil and gas industry. However, all the past methodologies are based on solvent extraction, filtration, and concentration. These traditional techniques are cumbersome, time-consuming, and suffer from analyst-to-analyst variability while producing data of limited value.

Today, analytical pyrolysis encompasses much more than simple flash pyrolysis of polymeric materials. Virtually any material (liquid or solid) can be characterized using an array of techniques, which are designed into the modern-day, multi-mode vertical micro-furnace pyrolysis system. Using the multi-mode micro-furnace pyrolyzer, volatiles, additives, oligomers, polar, polymeric, and heavier components can be analyzed. This technique broadens the range of organic chemical analysis by Gas Chromatography-Mass Spectrometry (GC/MS). Any solid sample can be analyzed "as is" without solvent, solvent extractions, or pretreatments prior to the analysis.

Pyrolysis GC/MS, shown in Figure 1, is a powerful and straightforward analytical technique comprised of a vertical micro-furnace pyrolyzer coupled directly with a GC/MS system. Using this technique, a sufficient amount of heat reproducibly breaks down the organic bonds of a complex mixture into smaller, stable molecules referred to as pyrolyzates. These pyrolyzates and their relative intensities provide insight into the nature of the original material ("Pyrolysis," 2019).

This article demonstrates the capabilities of the micro-furnace pyrolyzer interfaced with a bench GC/MS system and the

1. Auto-Shot Sampler (AS-1020E)
2. Multi-Shot Pyrolyzer (EGA/PY-3030D)
3. Selective Sampler (SS-1010E)
4. MicroJet Cryo-Trap (MJT-1035E)
5. Ultra-ALLOY® metal capillary column
6. Vent-Free GC/MS adapter
7. F-Search (search engine and MS libraries)

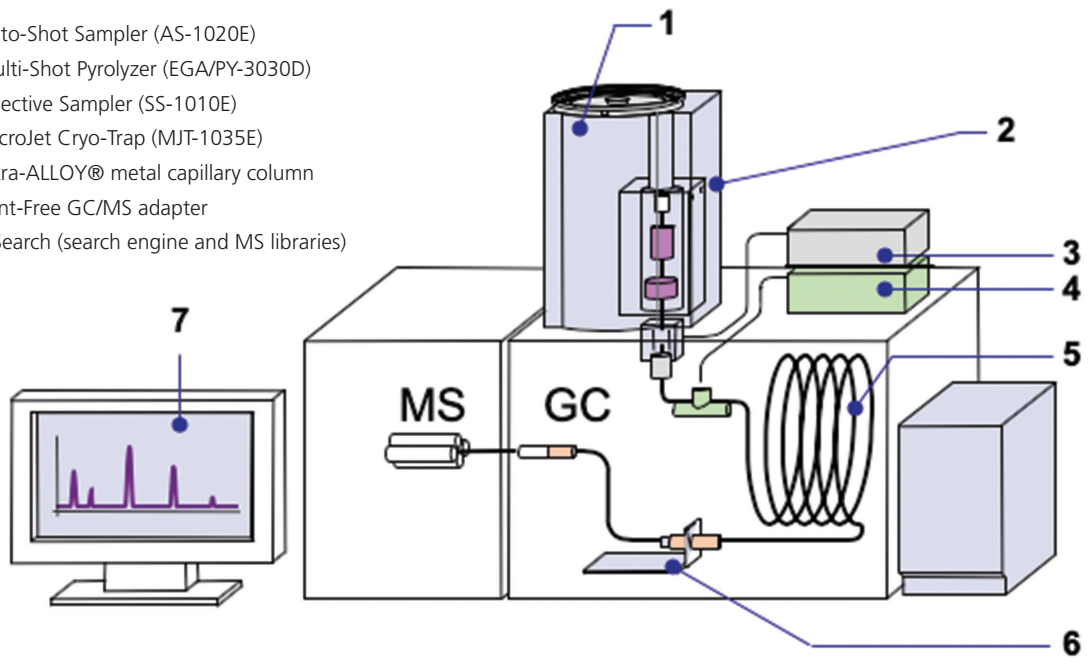

Figure 1. Pyrolysis GC/MS Configuration ("Multi-Functional Pyrolysis System," 2019)

modes of operations used for deformulation and comparison analysis of three different coals: soft coal, lignite coal, and sub-bituminous coal.

Sample preparation using Pyrolysis-GC/MS is simple and straightforward. There is no need for any solvent extraction or sample pretreatment. In this experiment, a small amount of each sample (100 to 200 micrograms) in solid form was placed in an easy to use inert sample cup for analysis.

The system configuration for this experiment is shown in Figure 1. It is important to mention that the vertical micro-furnace pyrolyzer performs single-step pyrolysis and it is directly connected to the GC inlet. There is no transfer line, no active site, and no cross-contamination. The sample introduction is nearly instantaneous. The sample is placed in the inert sample cup (Eco-cup) and is held at a near ambient temperature in helium. The micro-furnace is then preheated to the desired temperature that is precisely measured with a thermal couple sensor. The sample cup drops into the quartz pyrolysis tube where the sample is pyrolyzed rapidly and reproducibly. The pyrolyzates are deposited directly onto the analytical column as they are generated and then separated by GC for detection by MS. All surfaces in contact with the sample and pyrolyzates are either quartz or deactivated ("Multi-Shot Pyrolyzer," 2013).

The multi-mode micro-furnace pyrolyzer enables the user to perform multiple analytical techniques, such as Evolved Gas Analysis (EGA), Thermal Desorption (TD), Flash Pyrolysis (PY), Heart-Cutting (HC), Double-Shot (TD followed by PY), and Reactive Pyrolysis (RxPY). Frontier Laboratories has developed a series of techniques referred to as the "method map" to chemically characterize samples using the micro-furnace. These techniques are applicable to virtually any organic materials from volatiles to high molecular weight polymers. The "method map" provides the user with simple steps for determining the composition of an unknown sample.

The first step is Evolved Gas Analysis. To perform EGA, no separation column is used; a short, small diameter (2.5m, 0.15 mm id.) deactivated tube connects the injection port to the detector. The sample is dropped into the furnace, which is at a relatively low temperature (ca. 40-100˚C). The furnace is then programmed to a much higher temperature (ca. 600-800˚C). Compounds evolve continuously from the sample as the temperature increases. A plot of detector response versus furnace temperature is then obtained.

The EGA thermogram provides a clear picture of the sample complexity and thermal profile. Using extracted ion chromatograms, one can identify the EGA thermal zone where specific compounds of interest evolve from the sample. The example below contains two thermal zones of interest ("Evolved Gas Analysis (EGA)," 2019).

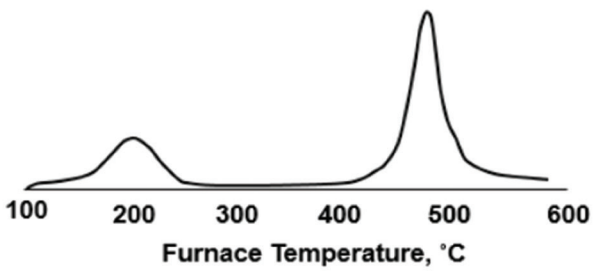

Figure 2. Example of an EGA Thermogram ("Evolved Gas Analysis (EGA)," 2019)

The EGA is then used to determine next steps in the evolution of the analytical method map. From Figure 2, one can learn about the volatile fraction of the sample by simply introducing the sample at 300˚C – only the compounds evolving below 300°C will come out from the sample and be transferred to the analytical GC separation column.

If there is interest in both the volatile fraction and higher boiling compounds, Double-Shot mode of operation using the micro-furnace can be utilized. Using Double-Shot mode, first, the volatile compounds are thermally extracted by dropping the sample into the furnace, which is at 300°C. During the GC analysis of the volatiles, the sample is lifted out of the furnace and rests at near ambient. Upon completion of the GC run, the GC oven is reset, and the pyrolyzer furnace temperature is raised to 550°C. The sample is dropped a second time into the furnace for pyrolysis. The Pyrolzates are directly transferred to the GC column for separation and then detection by the MS. This is called Double-Shot analysis as two analyses are performed on one sample, thermal desorption followed by flash pyrolysis ("Evolved Gas Analysis (EGA)," 2019).

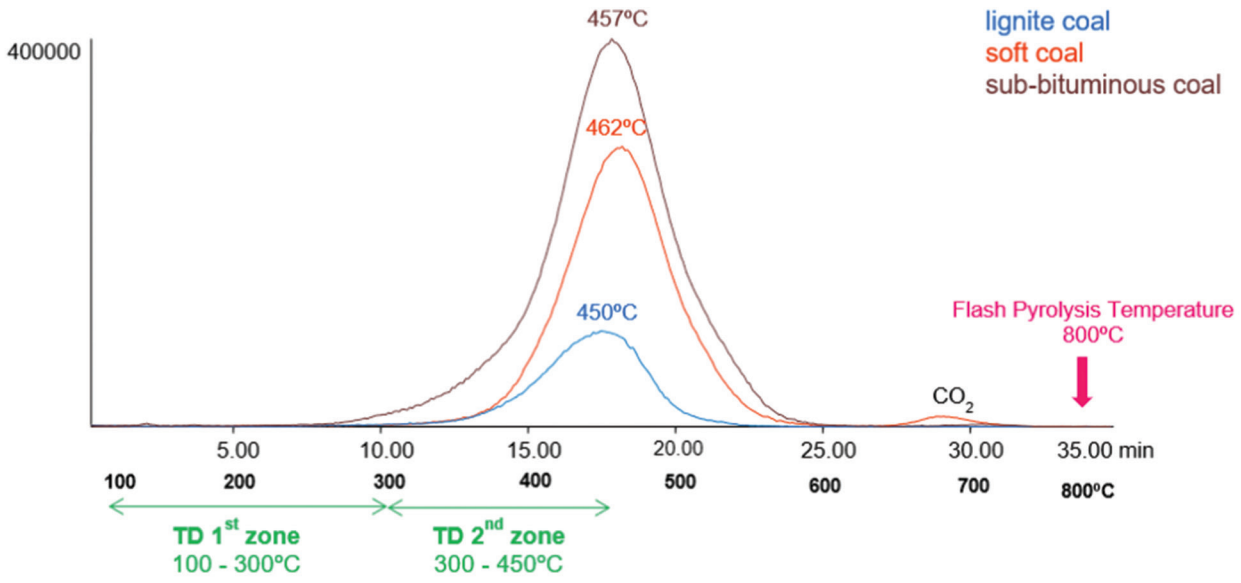

Figure 3. Overlaid EGA Thermograms with Peak Top Temperature (Shiono et al. 2013)

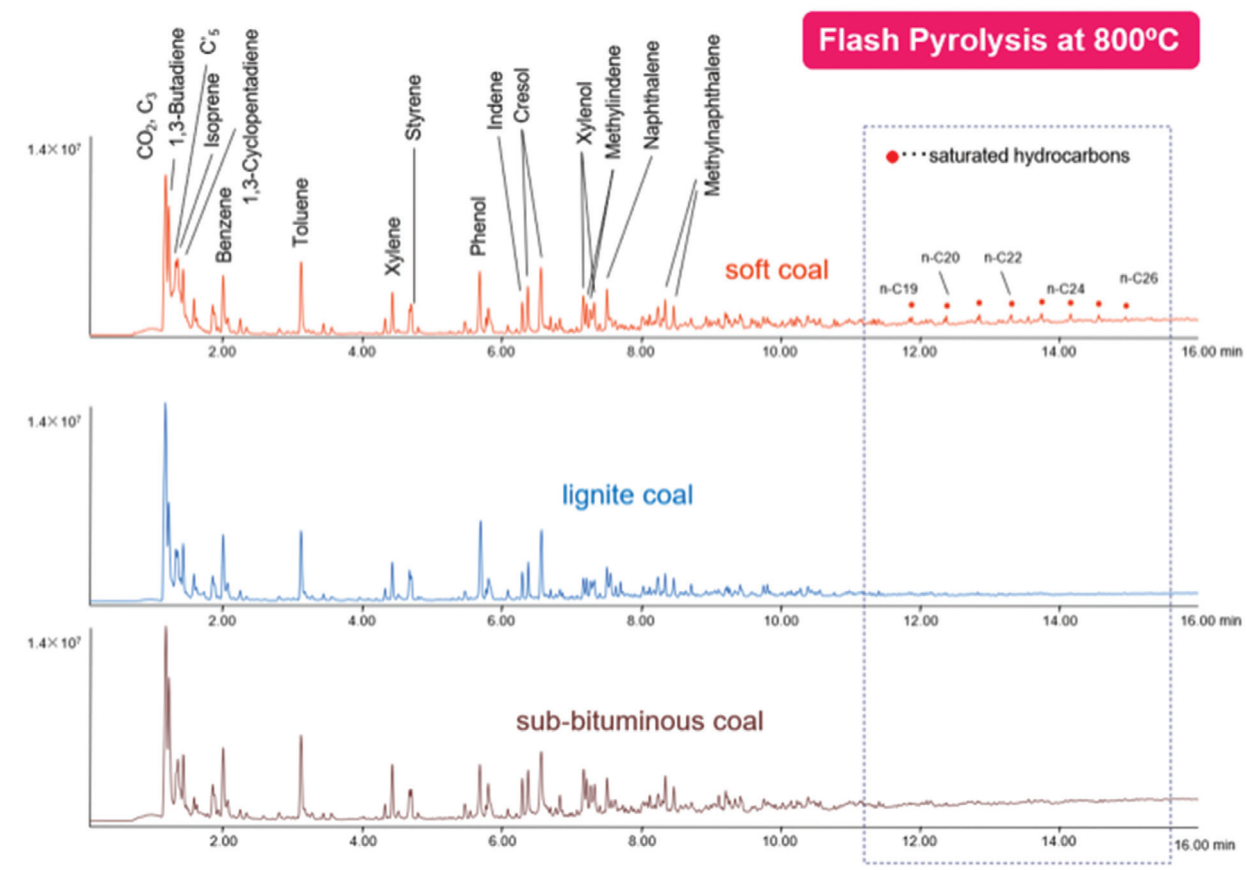

Figure 4. Flash Pyrolysis Pyrograms of Coal Samples (Shiono et al. 2013)

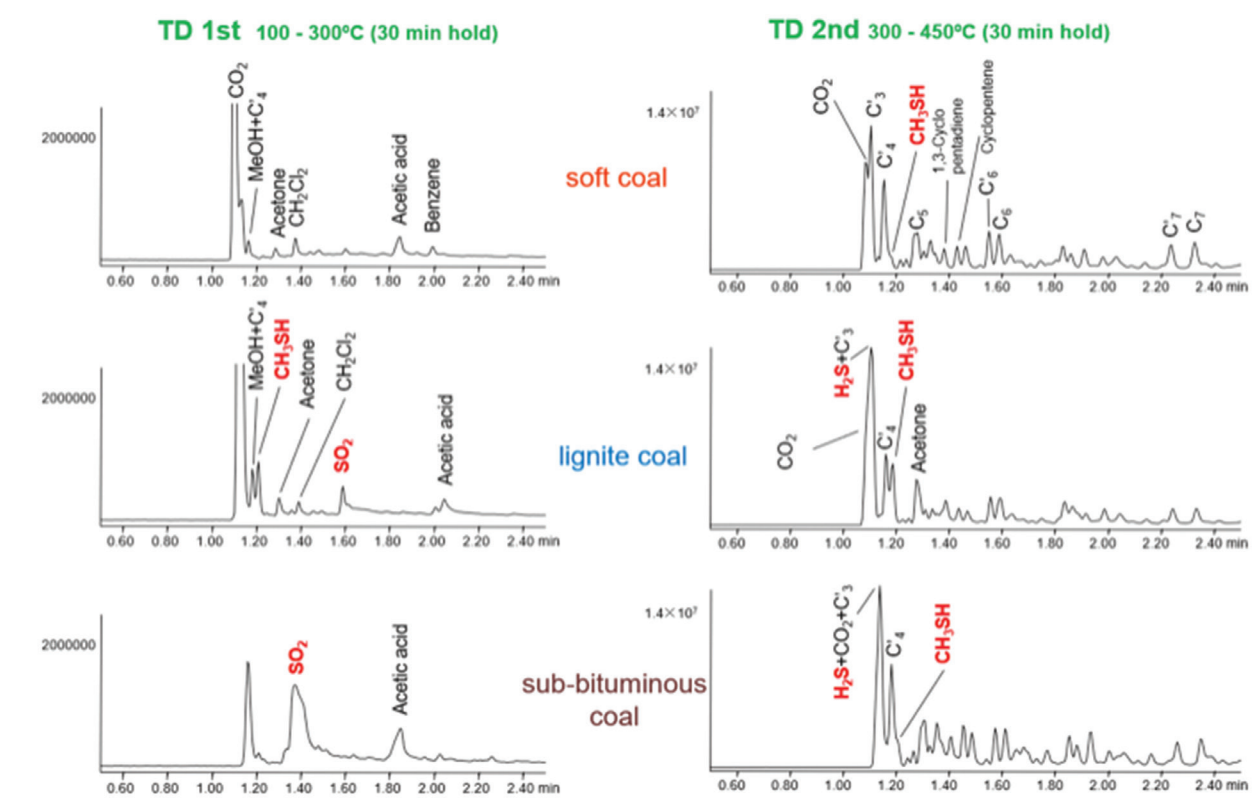

Figure 5. The Expanded View of 0.5-2.5 Minutes of TD Chromatograms (Shiono et al. 2013)

Experimental

To characterize the chemical composition of the coal samples, EGA was first performed from 100 - 800ºC (20 ºC/min) using the EGA deactivated tube (UADTM-2.5N, 2.5 m x 0.15 mm id). Figure 3 shows the overlaid EGA thermograms of coal samples and the differences in peak top temperature. The appropriate temperature zones for analyzing volatile and heavy/polymeric fractions of the samples were also identified using the obtained EGA thermograms.

To analyze the heavy fraction of the samples, flash pyrolysis was then performed at 800ºC using a separation column (Ultra ALLOY-5-30M-0.25F). Figure 4 shows the pyrograms and compounds identification. Hydrocarbon peaks between 12-15 minutes were observed in the soft coal.

Using the Thermal Desorption (TD) mode of operation, the volatile and light fraction of the samples were also analyzed. The first TD was performed from 100 to 300ºC and the second TD was from 300 to 450ºC. Figure 5 shows the expanded view of 0.5 to 2.5 minutes range of TD chromatograms with the peak identifications. The sulfur-containing compounds (SO_2, CH_3SH, and H_2S) were observed in lignite and sub-bituminous coal, whereas there was little indication of sulfur compounds in the soft coal (Shiono et al. 2013).

Conclusion

Using the micro-furnace pyrolyzer's different modes of operation, the chemical composition of coal samples was identified. A comparison analysis was also performed to reveal the minor differences in various types of coals. Although the coal samples showed similar EGA thermograms, the apex temperature and peak width were different. From the flash pyrolysis pyrograms, the hydrocarbon peaks were identified only in the soft coal. TD of the lignite and sub-bituminous coals identified sulfur-containing compounds.

Today, more analytical laboratories are integrating the multi-mode micro-furnace pyrolyzer into their mainstream analytical protocols due to the advantages and immediate quality improvements this technique provides. This technology provides the users with a clear picture of the sample's composition by identifying the thermal zones and the compounds in each zone.

Using the obtained EGA thermogram, one can simply program the micro-furnace with the appropriate temperature, such as Double-Shot and Heart-Cutting. This technique allows multiple analyses on a single sample while there is no need for any solvent and sample pretreatment as the sample is simply introduced into the GC/MS by the multi-mode pyrolyzer.

Compatible with major GC/MS systems, the multi-mode micro-furnace guarantees reproducibility, accuracy, and precision while the entire analysis is automated using the auto-shot sampler.

References

- A. Shiono, C. Watanabe, & I. Watanabe (2013). Coal Analysis. Frontier Laboratories Ltd. 4-16-20 Saikon, Koriyama, Fukushima, 963-8862 JAPAN (www.frontier-lab.com)
- Multi-Shot Pyrolyzer. (2013). Retrieved from http://www.frontier-lab.com/catalog/en/PY-3030D_E.pdf
- Pyrolysis. (2019). Retrieved from http://www.frontier-lab.com/english/pyrolysis/
- Multi-Functional Pyrolysis System. (2019). Retrieved from http://www.frontier-lab.com/english/multi-functional-pyrolysis-system/
- Evolved Gas Analysis (EGA). (2019). Retrieved from http://www.frontier lab.com/english/evolved-gas-analysis/

Author Contact Details

Rojin Belganeh, Technical Director-Frontier Lab Americas • 1001 South Dairy Ashford Rd Suite 100, Houston TX 77077

• Tel: +44 925.813.0498 • Email: rojin@frontier-lab.com • **Web: www.frontier-lab.com**

Co-authors: William Pipkin, Anna Shiono, Ichi Watanabe, Chu Watanabe - Frontier Laboratories Ltd.