Specac

Application Note

Analysis of Coal Samples in a High Temperature High Pressure Transmission Cell

High-Temperature
High-Pressure Cell

INSIDE: Find out how the HT/HP cell has been used to investigate the impact of heating coal samples on its oxygen content.

Introduction

In-situ analysis of materials at high temperature and pressure using infrared spectroscopy has become an indispensable method in modern material characterisation. Traditional methods are often not capable of obtaining satisfactory sample spectra of dark materials such as coal and graphite, where the main difficulties stem from poor light throughput, sample processing, data analysis, and baseline shifting. Coal is produced over millions of years from underground sediments subject to heat and pressure, in a process known as coalification. The resulting coals are ranked according to their total carbon content and heating value [1]. When analysing coal samples using Specac's tri-modal High Temperature High Pressure cell (HT/HP cell) in conjunction with FTIR, it quantitatively measures chemical composition and the extent of deterioration through absorbance change during oxidation at different temperatures. The absorbance changes to oxygenated functional groups, aliphatic C-H groups, and aromatic C-H groups are of particular interest when monitoring coal oxidation, commonly referred to as combustion. Coal's functional groups can be used to determine its storage, autoignition, and combustion properties, and ultimately its quality and price.

High optical throughput reaction chamber for IR analysis in multiple configurations: transmission, reflectance, and decomposition.

- Sealed sample chamber with controlled atmosphere.
- Temperature to 800 °C and pressure from vacuum to 68 bar (1000 psi).
- Converts to specular reflectance mode for opaque or reflective samples using external mirrors.
- Sample pans allow analysis of gases released from thermal decomposition of solids.
- Unmatched performance.
- Ideal for characterisation of coal, catalysts, resins/polymers, ceramics, and minerals

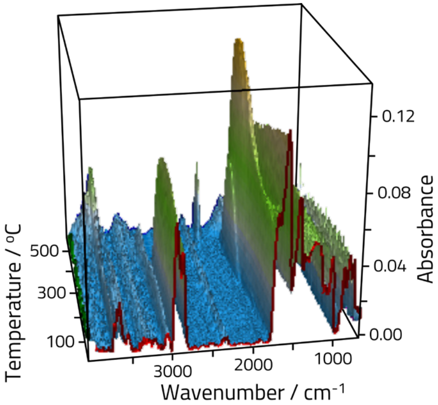

Figure 1: *HT/HP three-dimensional spectra showing the effect of temperature on chemical changes to a coal sample.*

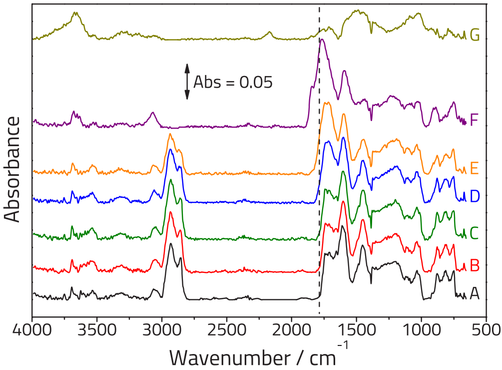

Figure 2: *FTIR spectra of characteristic temperature bands during coal oxidation: critical temperature (A); dry cracking (B); thermodynamic activity (C); growth rate (D); thermal decomposition (E); ignition point (F); and maximum mass loss rate (G). The dashed line shows the position of the trace shown in Figure 3.*

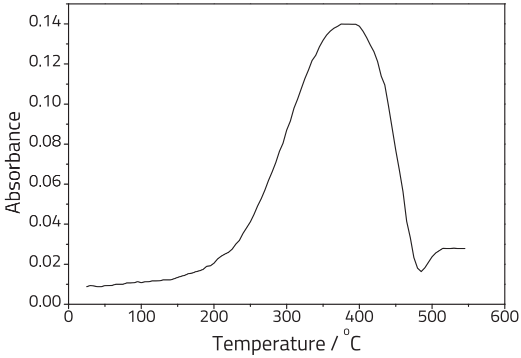

Figure 3: *In-situ infrared analysis of changes to carbonyl functional groups during coal oxidation showing the change in peak intensity at 1786 cm⁻¹ (see Figure 2).*

Experimental

1.5-2.0 mg of coal sample was weighed and dried under vacuum at 105 °C for two hours to remove moisture. The coal sample was then mixed with potassium bromide (KBr) powder and pressed into a pellet for analysis. For FTIR measurement, the sample was placed into the Specac HT/HP cell, which was then filled with a nitrogen atmosphere. Spectra were recorded in the 4000-500 cm^{-1} range with a resolution of 4 cm^{-1} and 32 scans on a commercially available spectrometer.

Results and Discussion

Coal contains a complex mixture of organic and inorganic species. Organic oxygenated functional groups found in coal include hydroxyls, carbonyls, ether, quinone rings, and other oxygenated heterocycles. These functional groups form complex bonds and display unique vibrational modes; some of these groups absorb infrared beam in the ~1300-1000 cm^{-1} region. A small percentage of the oxygen content of coal exists in carboxyl groups; the majority is found in hydroxyl groups and other oxygenates; the oxygen content in the latter contributes to half of the total oxygen content in coal [2].

In **Figure 1**, two sharp absorption bands at 2900 cm^{-1} and 2800 cm^{-1} are assigned to saturated aliphatic C-H; additionally a weaker band at 3050 cm^{-1} is attributed to unsaturated aromatic C-H. These bands are relatively stable as the temperature is increased up to about 400 °C, before rapidly decaying. Changes are also obvious in the fingerprint region, although assignment here is complex due to multiple overlapping features. At lower temperatures aromatic groups dominate the spectra in the 1550-1700 cm^{-1} region [3]. As the sample is heated features grow into the high energy side of these peaks assigned to oxygenate materials.

Figure 2 shows FTIR spectra measured at seven characteristic temperatures A-G of coal combustion which were determined by Thermogravimetric Analysis (not shown). The changes to functional groups occurring at each of these temperatures during combustion was monitored quantitatively by FTIR. The temperature dependence of functional groups was then probed by plotting band intensity vs temperature as shown for the carbonyl functional group in **Figure 3**.

As the temperature is increased from room temperature up to 385 °C carbonylation occurs via a free radical reaction mechanism between the coal and oxygen trapped within the disc. Above 400 °C subsequent polycondensation (generating water and carbon dioxide), bond cleavage, and then fragmentation into small molecules causes a decrease in the carbonyl content of the coal.

Increasing the concentration of oxygenated functional groups in coal increases the combustibility of the coal, but also results in a higher risk of autoignition and spontaneous combustion; the lower the concentration, the lower the volatile matter content in coal, which ultimately determines its increase in coal rank or extent of coalification as the fixed carbon ratio increases.

Conclusion

The Specac HT/HP cell plays a significant role in monitoring coal's change in chemical composition during combustion. A variety of parameters such as the coal's storage ability, oxygen absorbability, combustibility, and subsequently coalification ranking of samples from different geographical locations across the globe can be determined with ease.

References

[1] https://www.eia.gov/energyexplained/coal/

[2] X. You, H. Wei, X. Zhu, X. Lyu & L. Li, *Molecular Physics*, **116**, (2018), 1670-1676, DOI: 10.1080/00268976.2018.1441465

[3]https://www.specac.com/en/resources/infrared-frequency-tool

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