TA Instruments

Thermal Analysis & Rheology

KINETIC PARAMETERS OF OVERLAPPING COAL DECOMPOSITION REACTIONS BY MTGA™

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When coal is heated in the absence of air, it looses weight in a series of steps. The lowest temperature weight loss is due to water which volatilize below 200 °C. Between 200 and 900 °C, volatile (hydro)carbons are evolved. If the pyrolyzed coal is then exposed to air at 900 °C, fixed carbon is burned leaving a non-combustible ash residue. The determination of the four components (water, volatile carbon, fixed carbon and ash) is called the proximate analysis of coal and is quickly and easily performed using thermogravimetry and ASTM standard E 1131 [1].

The kinetic parameters for a single reaction weight loss, including activation energy, pre-exponential factor and reaction order, are easily obtained using the traditional variable heating rate Flynn and Wall method [2,3]. This is approach is embodied in the TA Instruments TGA Decomposition Kinetics software package.

The volatile carbon weight loss in coal, however, is not associated with a single weight loss but, rather, with several. Pan and co-workers, for example, have observed and determined kinetic parameters for at least four (4) different unresolved weight loss regions within the volatile carbon region [4].

The determination of kinetic parameters for unresolved and overlapping weight losses is difficult using the variable heating rate approach as resolution decreases as the higher heating rates required by the method are used. The resolution decrease causes the shoulders to disappear and partially resolved peaks to merge.

Modulated Thermogravimetry (MTGA™) is a useful tool for determine kinetic parameters of closely spaced and overlapping weight loss reactions. In MTGA, a sinusoidally varying temperature program is superimposed over the transitional constant heating rate temperature program. This produces a

sinusoidal change in the rate of the weight loss in the region of a reaction. Discrete Fourier transformation is used to deconvolute the temperature and weight loss signals so that kinetic parameters are obtained continuously and in real time. This permits the display of activation energy, for example, at any point along the thermal curve as a function of temperature, weight loss or conversion. Typical MTGA experimental conditions include an underlying heating rate of 2 °C/min, an oscillation amplitude of ±4 °C and a period of 200 sec.

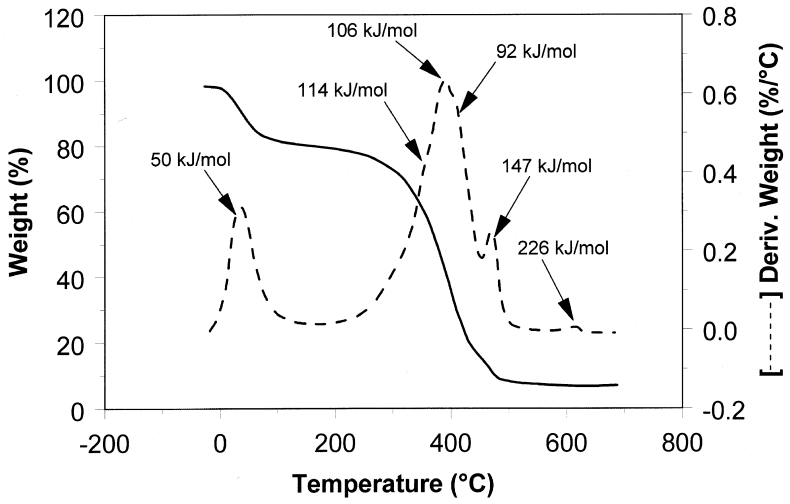

Figure 1 shows the weight loss and rate of weight loss profiles for a coal sample. The volatile carbon weight loss between 300 and 500 °C with peaks in the derivative curve seen at 374, 447 and 580 °C and shoulders or inflections at 325 and 391 °C. The MTGA generated continuous activation energy may be marked for any point in the weight loss region. The determined activation energy is that for the mix of reactions occurring at the particular temperature and conversion.

In summary, MTGA provides a tool for continuously determining activation energy throughout a weight loss region yielding kinetic parameters at any point. This ability permits the determination of activation energies for unresolved and overlapping transition as well as for well resolved peaks.

References

[1] E 1131 "Standard Test method for Compositional Analysis by Thermogravimetry", Ann. Book of ASTM Stand., Vol. 14.02, ASTM, West Conshohocken, PA.

[2] Flynn, J.H.; Wall, L.A., Polym. Lett., 4, 323 (1966).

[3] E 1641 "Standard Test Method for Decomposition Kinetics by Thermogravimetry", *Ann. Book of ASTM Stand.*, Vol. 14.02, ASTM, West Conshohocken, PA.

[4] Serageldin, M.A.: Pan, W-P.; Thermochim. Acta, 76, 145-160 (1984).

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