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APPENDIX 7

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Huang, H.;Wang, K.; Wang, S.; Klein, M. T.; Calkins, W. H. "Distillation of Liquid Fuels by Thermogravimetry"

Wang, K; Wang, S.; Huang, H; Klein, M. T.; Calkins, W. H. "A Novel Smoothing Routine for the Data Processing in Thermogravimetric Analysis.

Huang, H.; Wang, K.; Wang, S.; Klein, M. T.; Calkins, W. H. "Applications of the Thermogravimetric Analysis in the Study of Fossil Fuels"

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A NOVEL SMOOTHING ROUTINE FOR THE DATA PROCESSING IN THERMOGRAVIMETRIC ANALYSIS

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Key words: smoothing, differentiation, thermogravimetric analysis

INTRODUCTION

Thermogravimetric (TG) techniques have been used in characterizing fossil fuels (1-4) and in studying coal liquefaction kinetics, mechanisms, and processes (5,6). The TG techniques have been providing sensitive, rapid, and reproducible measurements for those purposes.

The primary output of thermogravimetric analysis (TGA) is in the form of a three-column matrix of time, temperature, and mass (or mass%). The first derivative of the TG (i.e. DTG) is capable of revealing fine details of the processes occurring more clearly for sample characterization (2,7) and/or as an input variable for further analysis, for example, in the SimDis (Simulated Distillation) TG technique (8).

There always is a limitation on the sensitivity of the TGA instrument. This is particularly true for those analyses run at either very low heating rates or very slow DTG decay experiments, where small changes in mass occur. Therefore, smoothing and filtering of these large data sets to obtain noise-free DTG curves are crucial in those TGA applications.

Several methods have been developed for smoothing and differentiation of experimental data (9-15). The objective of this paper is to present a novel and specific method for smoothing and differentiation of thermogravimetric data. The principle of the method is based on the characteristics of the TG data (e.g. time vs. mass). Linear regression and error analysis are used in the smoothing and filtering routine. The computer program required is simple and effective. The method used in the program promises auto-convergence. The reported technique in this paper could also be applied to other analytical instrumentation.

EXPERIMENTAL

The thermogravimetric analyzer (TGA) was a Model 51 TGA (TA Instruments, New Castle, Delaware). The program of manipulation of the TG variables, such as heating rate, type of purge gas and its flow rate, and final (or step) temperature, was determined by the objectives of the particular experiment. The output matrix of a TG scan (time, temperature, mass) was recorded by computer. The digitized data were then transferred into DOS (ASCII) format using a program provided by TA Instruments. The ASCII format data were loaded into MATLAB (The MathWorks, Inc.) and processed using a MATLAB routine.

METHOD OF SMOOTHING AND DIFFERENTIATION

The General Problem. The random errors which, regardless of their source, are characterized as noise are always present in the TGA measurements. This background noise reduces signal-to-noise ratio, resulting in decreasing sensitivity. This is particularly true when the DTG is the objective result of a TG scan. Figures 1 and 2 show the DTG plots for TG scans run at a very low heating rate (1°C/min) and a very slow DTG decay, respectively. These DTG plots were obtained from numerical differentiation of the original TG data. As shown in Figures 1 and 2, it is necessary for the investigator to remove the noise as much as possible without, at the same time, distorting the experimental data, especially for those processes where small changes in mass occur. Smoothing and filtering of these thermogravimetric data to obtain the noise-free differentiation (DTG curve), therefore, are required in the TGA applications.

The Characteristics of the TG Data (time vs. mass). A TG curve of the Illinois #6 coal at a heating rate of 1 °C/min in 100 cm^3(STP)/min nitrogen is shown in Figure 3. Thirty one data points of (t,w) taken from Figure 3 are plotted in Figure 4. The plot shows a very good linearity between the mass and time. In general, this is always true for a certain short time interval of a TG scan. It is this characteristic that is used to develop a method for smoothing and differentiation of the TG data.

Smoothing and Differentiation by Linear Regression and Error Analysis. One of the simplest ways to smooth fluctuating data is by a n-point ($n=2k+1$; $k=1,2,3,\ldots$) moving average procedure. In this method, a fixed odd number ($2k+1$) of data points are taken to obtain the average for the center point, ($k+1$)th point, of the group. To move on, the first point in the group is dropped, the next point at the end of the group added, and the process is repeated. In statistics, noises in the data file are not filtered by this simple average procedure.

Consider a group of n (for example, n = 11) points of (t, m) taken from a TG file and plotted in Figure 5. Based on the characteristics of the TG data discussed in the previous section, a linear regression can be performed in this group by

$$m = a + b \times t \qquad (1)$$

and represented by the solid line in Figure 5. The obtained linear regression parameters (i.e., *a* and *b*) can be used to estimate the *m* (mass) at each *t* (time) in the group. The errors (e) between the linear regression ($m_{cal.}(i)$) and experimental data ($m_{exp.}(i)$) in the group are defined as

$$e(i) = m_{cal.}(i) - m_{exp.}(i) \qquad (2)$$

The statistical parameters of the errors for this group, e.g. mean (e_{mean}) and standard derivation (e_{std}) of the errors, are calculated by:

$$e_{mean} = \frac{\sum_{i=1}^{i=n} e(i)}{n} \qquad (e.g.\ n = 11)$$

$$e_{std} = \frac{\sqrt{\sum_{i=1}^{i=n} (e(i) - e_{mean})^2}}{n - 1} \qquad (3)$$

To eliminate the noise from this group, standard deviation of the errors can be used as a criterion to define the filter range. This is plotted as dashed-lines in Figure 5. In detail, if the experimental data point locates outside the filter range, i.e. $e_i > e_{std}$, it is considered as a noise in the group. To filter this noisy point, it is replaced by an estimated value of $m_{cal.}(i)$ using the linear regression. This filter procedure can be used on each point in the group and a new data set can be formed. This new data set is plotted in Figure 6. The points with "x"in Figure 6 represent the filtered data. Linear regression can be again carried out in this new data group, followed with upgraded error analysis and filtering process. The linear regression, error analysis and the filter procedure are repeated until the standard deviation of the errors is below a predetermined value of $e_{std,\ o}$. In this study, a relative standard deviation of the errors, re_{std}, rather than e_{std}, has been used for evaluating the calculations. This relative standard deviation of the errors is defined as e_{std} times the absolute value of the slope (DTG) of the linear regression, i.e.,

$$re_{std} = abs(b) \times e_{std} \qquad (4)$$

This relative standard deviation of the errors used as a criterion to evaluate calculations can insure the precision of very slow process (i.e., very low DTG scan). It has been found that $re_{std,o}$ set at 10^{-5} gives very satisfactory results. The final regression results are used to estimate the smoothed mass and differentiation for the center point of $t_{(k+1)}$, i.e.,

$$m_{k+1} = a + b \times t_{k+1} \qquad (5)$$

Since the standard deviation of the errors constantly decreases with iterations, the computation method used in the program promises auto-convergence.

For a TG analysis, the n-point smoothing, filtering and differentiation routine has been moved in the data file similarly as the moving average method which has been described earlier. A scheme of the computation routine is illustrated in Figure 7. For the "end-points" (i.e., either the initial or the final k points in the data file), a different method has to be used to evaluate them. One of the simplest ways to handle this "end-points" problem is to throw them away, since these end-points usually are not important or not of interest. In this study, the end-points have been simply assigned by their original values. If the "end-points" become important, a much more sophisticated method developed by Leach et al. (10) could be used.

APPLICATIONS

SimDis TGA. A SimDis TGA method for determining the boiling point distribution of liquid fuels is reported elsewhere (8). Original DTG plot for a petroleum sample,light paraffinic vacuum distillate,is shown in Figure 2. To transfer the DTG decay into boiling point distribution, it is necessary to smooth the noisy DTG data. The results of n = 0- (i.e., original), 3-, 5-, 7-, 9-, and 11-point smoothing and filtering are illustrated in Figure 8. The more the data points used for smoothing and filtering, the smoother the DTG curve. However, at the same time, the more CPU or the longer computing time are required. More importantly, a large data number n used in smoothing increases the risk of distorting the experimental data. Eleven-point smoothing and filtering has been found to give the optimized results for the cases studied thus far. Figures 9a and 9b show the comparison plot (i.e., a plot including both smoothed results and original experimental data) and 11-point smoothing plot, respectively. The results indicate the smoothing and filtering method used in this study is very effective.

Characterization of coal structure. A representative TG scan on the Argonne Premium Illinois #6 bituminous coal, which was dried in a vacuum oven with a nitrogen purge at 105 °C for 48 hours before use, is shown in Figure 10. The two phases, i.e., 1) the heating rate to 950°C in nitrogen and hold for 7 min; and 2) the oxidation at 950°C, provided measures of VM, FC, and Ash, respectively. The differential of the weight loss (DTG) curve highlights the various TG processes more clearly. This becomes even more distinct and complex if the heating rate is slowed down to about 1 °C/min (2). However, the original DTG plot for this low heating rate shown in Figure 1 is so noisy that the processes involved in the TG scan could not be distinguished. The comparison plot and the 11-point smoothing results for this low heating rate scan are shown in Figures 11a and 11b, respectively. The processes involved in the TG pyrolysis of the coal at this low heating rate, as shown in Figure 11b, are very clearly distinguished. The low temperature peak represents the loss of residual moisture below 200 °C. The main Volatile Matter peak starts at 350-400 °C and actually consists of three or perhaps four individual weight loss processes. The large peak is broad and probably consists of a number of pyrolysis processes. The well defined peak at 571 °C is tentatively identified as due to pyrite decomposition to pyrrhotite and sulfur because this peak is absent in coals containing little or no pyrite. Also, the decomposition temperature corresponds closely to that reported for pyrite (16). Two other small peaks are not yet identified but are fairly broad. They disappear gradually during coal liquefaction (5).

With this smoothing and filtered method, the sole function of the computation is to act as a filter to smooth the noise fluctuations and hopefully to introduce no distortions into the experimental data. The problem of distortion is quite difficult to assess. In Figures 1 and 2, there are small fluctuations in the raw data. Are these fluctuations real, or, as is more likely, are they just noise? The question can not be simply answered by taking just the data from a single run. However, if two or three runs were taken, they gave the same results or, more characteristically, in same patterns. These indicated that the fluctuations are due to the noise, since the random errors will not recur in exactly the same place in different runs. The results of duplicate tests on all samples inspected in this study suggest that the fluctuations are truly due to noise.

CONCLUSION

For a certain short interval of a TG scan, the correlation between the mass and time is linear. A smoothing and filtering routine based on the use of linear regression and error analysis has been developed and successfully applied in the thermogravimetric data processing. This method provides a filter to smooth the noise fluctuations and, at the same time, to introduce no distortions into the TGA experimental data. The computer program required is quite simple and effective. The method used in the program promises auto-convergence.

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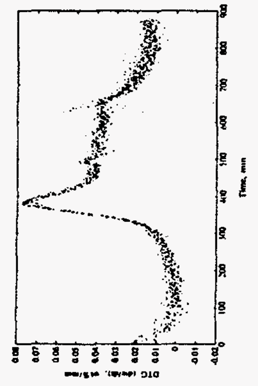

Figure 1 DTG of Illinois #6 coal pyrolysis at 1 C/min

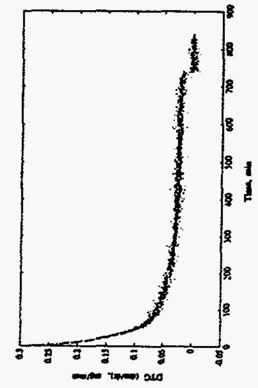

Figure 2 DTG decay of a SimDis TGA scan on a liquid fuel

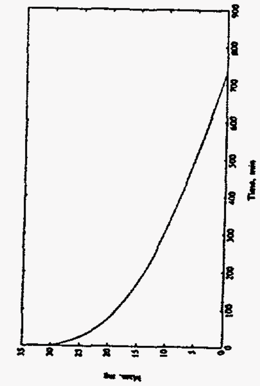

Figure 3 TG curve of Illinois #6 coal pyrolysis at 1 C/min (only volatile portion)

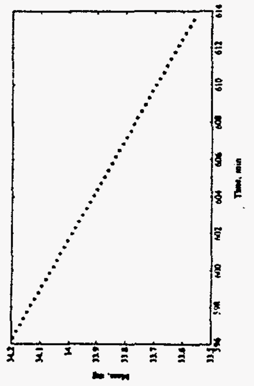

Figure 4 Characteristic of mass vs time in a TG scan (Thirty-one data points taken from Figure 3)

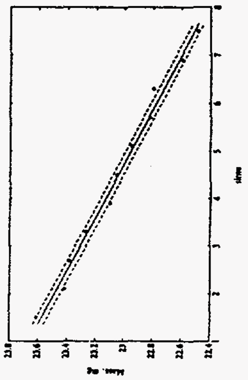

Figure 5 Mass vs time for a n-point group

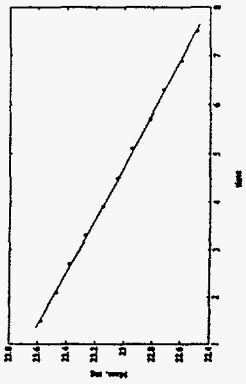

Figure 6 Mass vs time for a filtered n-point group

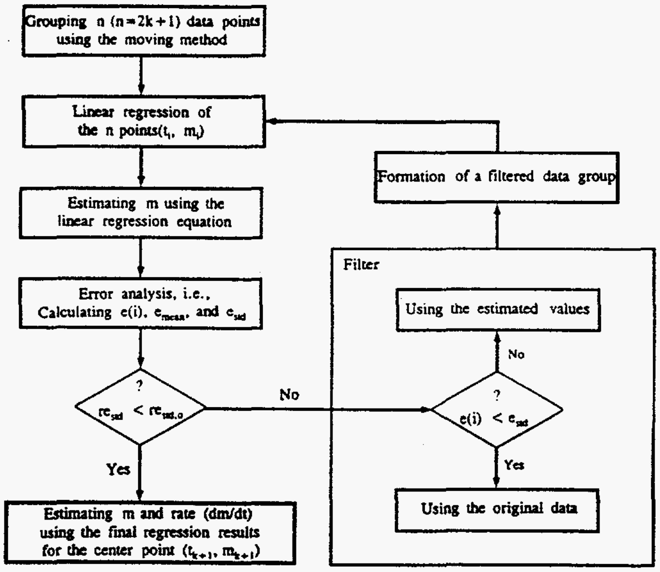

Figure 7 Flow-sheet of the n-point smoothing and filtering procedure

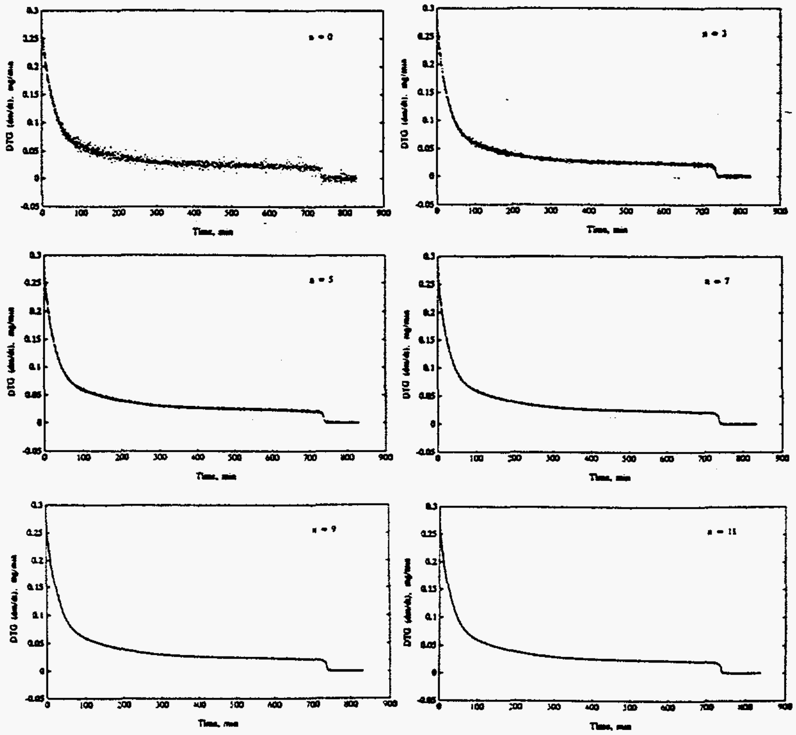

Figure 8 The results of n = 0-, 3-, 5-, 7-, 9-, 11-point smoothing and filtering

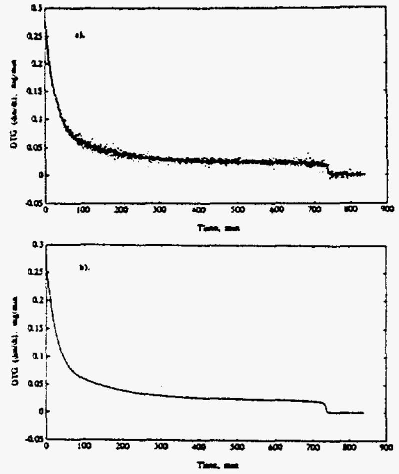

Figure 9 Visualization of n-point smoothing and filtering of the DTG at very slow heating rate shown in Figure 1: a). comparison plot; b). 11-point smoothing and filtering plot

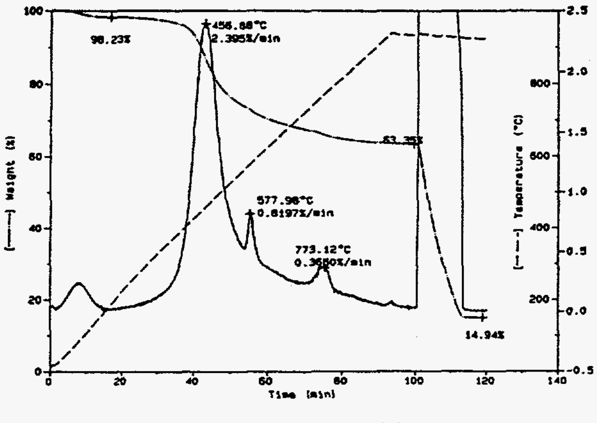

Figure 10 A TG scan of Illinois #6 coal at 10 C/min

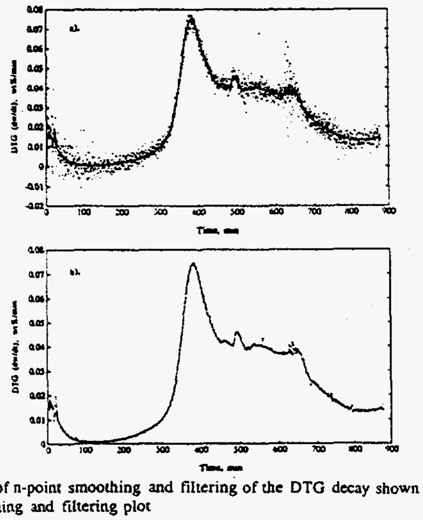

Figure 11 Visualization of n-point smoothing and filtering of the DTG decay shown in Figure 2: a). comparison plot; b). 11-point smoothing and filtering plot