Thermochimica Acta, 95 (1985) 33–40
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A COMPUTER PROGRAM SYSTEM FOR KINETIC ANALYSIS OF NON-ISOTHERMAL THERMOGRAVIMETRIC DATA. I. DATA ACQUISITION AND PREPARATION FOR KINETIC ANALYSIS *

JOHN P. ELDER **

Institute for Mining and Minerals Research, Kentucky Center for Energy Research Laboratory, P.O. Box 13015, Lexington, KY 40512 (U.S.A.)

(Received 25 April 1985)

ABSTRACT

FORTRAN software is described which enables the generation of rate of weight change data (DTG) from percentage weight change measurements (TG), obtained under non-isothermal conditions. The program also transposes this information into the dimensionless extent and rate of reaction at unit temperature intervals by means of a cubic spline interpolation. A simple search routine identifies all DTG spikes in the thermogravimetric record, and the temperature and extent of reaction at which the rate attains its maximum value. This total information serves as input data for the kinetic analysis software to be discussed in part II of this communication. An example of the application of this program to the pyrolysis of bituminous coal is presented.

INTRODUCTION

Recent experimental work on the pyrolysis of fossil fuels [1,2] in this laboratory and theoretical calculations simulating multiple reaction processes [3] have emphasized the need for computer software enabling the kinetic analysis of non-isothermal thermogravimetric data (TG/DTG). Such analyses are simplified if the experimental data is first transposed into the dimensionless extent and rate of reaction, α and $\mathrm{d}\alpha/\mathrm{d}t$, respectively.

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \tag{1}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{-1}{W_0 - W_\infty}\frac{\mathrm{d}W}{\mathrm{d}t} \tag{2}$$

where W_0, W_∞ and W represent the initial and final sample weights (or

* To be presented at the 14th North American Thermal Analysis Society Conference, San Francisco, CA, September 15–18, 1985.

** Present address: Merck and Co. Inc., P.O. Box 2000, R50D-101, Rahway, NJ 07065, U.S.A.

0040-6031/85/$03.30

weight percentages), and the instantaneous value at time t after the heating program is initiated, respectively.

Data acquisition is simplified if, rather than recording the DTG signal, it is calculated by differentiating the recorded weight change data, i.e., the TG signal. Such a calculation has a further advantage. At high heating rates, due to the finite time constant of the differential amplifier in the instrument, the DTG signal can be distorted. This may be demonstrated by monitoring the DTG signal of the effective weight change as a Curie Point magnetic standard undergoes the ferro- to diamagnetic transition at ever-increasing heating rates. The calculated DTG values are true derivatives. The differentiation may be accomplished by use of a cubic spline calculation, which, furthermore, allows the smoothing of the input TG data [4,5].

This paper describes a general FORTRAN program which transforms experimental digitized data into a form amenable for kinetic analysis, the details of which will be described in part II of this communication.

EXPERIMENTAL PROCEDURE AND COMPUTER SYSTEM

The procedure for preparing data for kinetic analysis, although quite general, has been developed specifically for treating non-isothermal thermogravimetric data generated using the Perkin-Elmer TGS-2/System 4 operated using the temperature control procedure previously described [6]. The analog TG data (percent of initial weight) is first amplified a hundred-fold using a high-input impedance dc amplifier, then digitized and transferred at appropriate time intervals to magnetic tape by means of a Mettler CT data acquisition system. At the conclusion of a series of runs, the data are then transferred, off-line to the in-house VAX 11/780 super mini-computer (Digital Equipment Co., Maynard, MA), where they are stored under the file name "Tgin". All further interaction with the computer is effected via a VT125 video display terminal (Digital Equipment Co.). The computer has a full-fortran compiler whose specifications adhere to ANSI-FORTRAN X3.9–1978, commonly referred to as FORTRAN-77. All final output data from the program are stored in the computer under the appropriate file name, where they are either printed out or used as input in the subsequent kinetic analysis.

DATA TRANSPOSITION—PROGRAM TGDATCON

Figure 1 shows a schematic of the overall program. It incorporates a published routine, CUBSPL [7], which performs a one-dimensional cubic spline interpolation (see Gerald [4] for details of this procedure). COEFF1 and TERP1 are the two major subroutines of the CUBSPL program,

TGDATCON

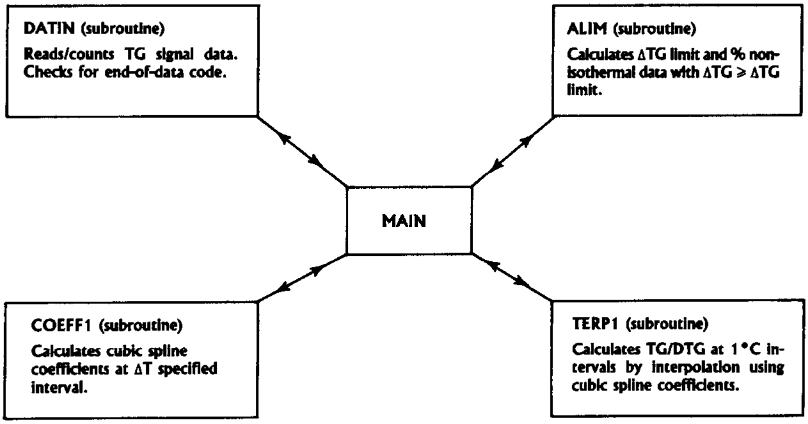

Fig. 1. Schematic of program TGDATCON.

performing the indicated functions. TG and the first derivative DTG may then be calculated at any integral temperature between the lower and upper limits. Subroutine DATIN reads in the experimental TG data, recorded at known temperature intervals, usually unity, stored on tape. ALIM is a subroutine which summarizes the data smoothing resulting from the interpolation. By comparing the actual and calculated TG values, a ΔTG limit is set such that no more than 1% of all the data lie outside the limit. One selects the ΔT interval for use in COEFF1 such that, following the interpolation calculations in TERP1, the ΔTG limit is within reasonable bounds (~ 1–2% of the experimental TG value), and also that < 5% of all generated DTG values are "spikes". The optimum cubic spline interval may quickly be found by trial and error.

The flow chart of the main program is shown in Fig. 2 and is self-explanatory. The experimental TG data, recorded at time intervals corresponding to unit temperature interval for a series of experimental runs at different heating rates, are read in from the Tgin file. Calculated TG and DTG data, α, $d\alpha/dt$ and $d\alpha/dT$ values at selected intervals (5 or 10°C, dependent upon the lower and upper temperature limits), are stored in the "Tgout" file available for subsequent print out. If a DTG spike is recognized, no matter how minor, this line of information is stored in Tgout, and on printing, an asterisk will be placed to the immediate right of the $d\alpha/dT$ value. If, at any temperature, the difference between the experimental and calculated TG values exceeds the ΔTG limit, this line of information is stored in Tgout, and on printing, an asterisk is printed one space to the right of the $d\alpha/dT$ value. At 1°C intervals, T, $1-\alpha$ and $d\alpha/dt$ values are stored sequentially in the "Alpha" output file. At the conclusion of each run, the heating rate, β, α_{max}

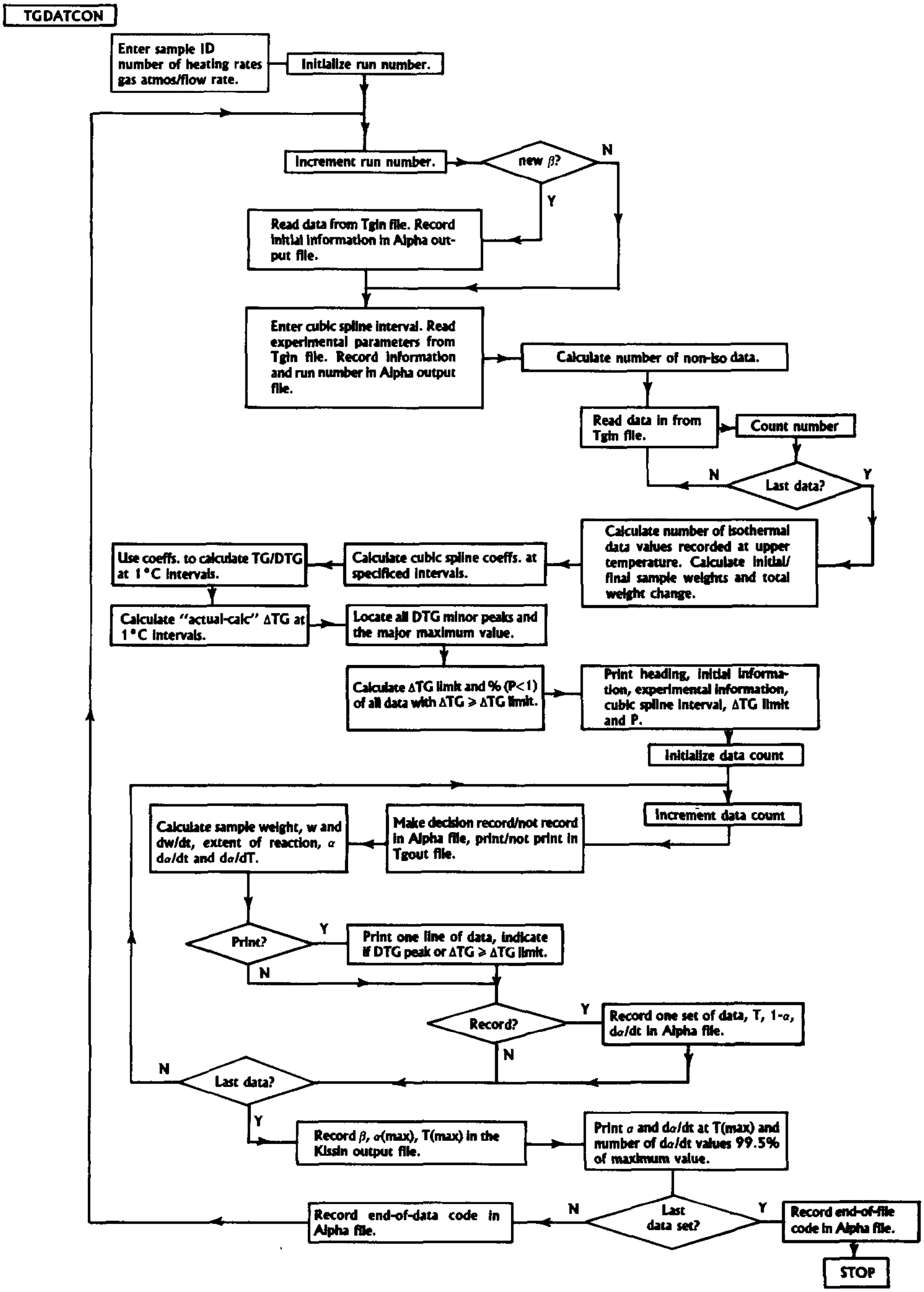

Fig. 2. Detailed flow chart of program TGDATCON.

and T_{max} values are stored in the "Kissin file". Both the Alpha and Kissin files of information are used as input data for the subsequent kinetic analysis. Any isothermal TG data recorded at the upper temperature limit are ignored in generating the Alpha file.

EXAMPLE OF PROGRAM APPLICATION—COAL PYROLYSIS

In order to demonstrate the general applicability of this procedure, data pertaining to coal pyrolysis, presented [8] but hitherto unpublished, have been used as input. Figure 3 shows typical TG/DTG analog curves characterizing the loss of volatile material as a typical bituminous coal is pyrolyzed at 5 (A) and 10°C min^{-1} (B). As is seen, such coals lose only about 35% of their initial weight. Table 1 shows part of the printed output (Tgout file) from program TGDATCON, at 10°C intervals. The second column shows the 100 × amplified TG signal (100% = 10 mV in the Perkin-Elmer TGS-2/System 4). In this example, a 25°C cubic spline interval was used to generate the interpolation coefficients. The ΔTG limit was calculated to be 1.3 mV and only 0.82% of the data lie above the limit. In this space-limited print-out, four DTG spikes are indicated with asterisks; data numbers 2, 91, 718 and 800. The asterisk for data number 384 indicates T_{max} and α_{max} as shown at the base of the table. The second position asterisk, data number 416, indicates that the difference between the calculated and experimental TG values at 465°C is greater than the 1.3 mV limit.

In order to check on the sharpness of the DTG peak, data at 1°C intervals 10°C above and below T_{max} are printed, and the number of $d\alpha/dt$ values within 99.5% of $(d\alpha/dt)_{max}$ is indicated at the bottom. The dots on the analog curves in Fig. 3 are the calculated TG/DTG values from Table 1. Although at 5°C min^{-1} the analog and calculated rate of weight loss data are in agreement, at 10°C min^{-1} there is a noticeable difference, particularly as T_{max} is approached. The distortion becomes more noticeable with further

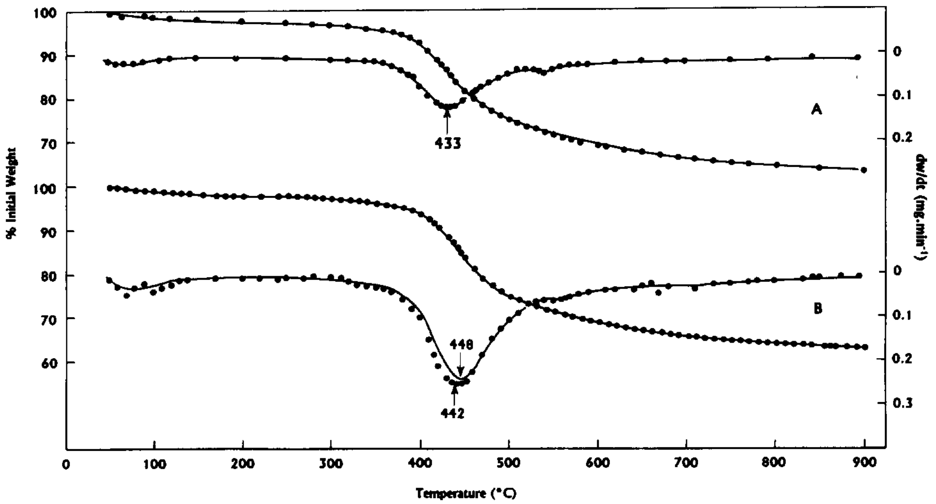

Fig. 3. Experimental and calculated TG/DTG data for the pyrolysis of a West-Kentucky #9 high volatile B bituminous coal at 5°C min^{-1} (A) and 10°C min^{-1} (B).

Table 1

Thermogravimetric Data: Sample: *West Kentucky No. 9, -60 mesh HVB Bituminous Coal* **Date:** *September 22, 1981*
Experimental Conditions: *From 50.0°C to 900.0°C at 5.0°C/min. in 100.0 ml/min. Nitrogen* **Run Number:** *1*
Weight Data: Initial: *9.720 mg (0.000 mg suppressed) recorded at 12.0 second intervals on the 10 mg range*
Cubic Spline Temperature Interval: *25°C "Actual-Calculated" Difference TG Signal Limit for Print-Out 1.300 0.82% Above*

Number	Signal (mv)	Temperature (°C)	Sample Wt. (mg)	Rate of Wt. Change (mg/min.)	α	$1-\alpha$	$d\alpha/dt$ (min^{-1})	$d\alpha/dT$ ($°C^{-1}$)
1	997	50	9.6908	0.0000	0.0081	0.9919	0.0000	0.0000
2	996	51	9.6873	1.7649E-02	0.0090	0.9910	4.8811E-03	9.7622E-04*
11	993	60	9.6556	1.7576E-02	0.0178	0.9822	4.8609E-03	9.7217E-04
21	989	70	9.6206	1.7354E-02	0.0275	0.9725	4.7995E-03	9.5991E-04
31	986	80	9.5864	1.6629E-02	0.0370	0.9630	4.5990E-03	9.1980E-04
41	983	90	9.5560	1.3266E-02	0.0454	0.9546	3.6689E-03	7.3378E-04
51	981	100	9.5353	6.9097E-03	0.0511	0.9489	1.9109E-03	3.8219E-04
61	980	110	9.5278	1.3848E-03	0.0532	0.9468	3.8299E-04	7.6598E-05
71	980	120	9.5267	5.1691E-04	0.0535	0.9465	1.4296E-04	2.8591E-05
81	979	130	9.5229	3.4025E-03	0.0545	0.9455	9.4099E-04	1.8820E-04
91	978	140	9.5145	4.6210E-03	0.0568	0.9432	1.2780E-03	2.5560E-04*
101	978	150	9.5062	3.2692E-03	0.0591	0.9409	9.0414E-04	1.8083E-04
374	877	423	8.5314	1.1348E-01	0.3287	0.6713	3.1383E-02	6.2767E-03
375	875	424	8.5086	1.1449E-01	0.3350	0.6650	3.1664E-02	6.3328E-03
376	873	425	8.4856	1.1544E-01	0.3414	0.6586	3.1927E-02	6.3854E-03
377	870	426	8.4624	1.1630E-01	0.3478	0.6522	3.2165E-02	6.4329E-03
378	868	427	8.4390	1.1704E-01	0.3543	0.6457	3.2370E-02	6.4740E-03
379	865	428	8.4156	1.1767E-01	0.3608	0.6392	3.2543E-02	6.5085E-03
380	863	429	8.3920	1.1818E-01	0.3673	0.6327	3.2683E-02	6.5366E-03
381	860	430	8.3683	1.1857E-01	0.3738	0.6262	3.2791E-02	6.5581E-03
382	858	431	8.3446	1.1884E-01	0.3804	0.6196	3.2866E-02	6.5732E-03
383	856	432	8.3208	1.1899E-01	0.3870	0.6130	3.2909E-02	6.5818E-03
384	853	433	8.2970	1.1903E-01	0.3936	0.6064	3.2920E-02	6.5839E-03*
385	851	434	8.2732	1.1895E-01	0.4001	0.5999	3.2898E-02	6.5795E-03
386	848	435	8.2494	1.1876E-01	0.4067	0.5933	3.2843E-02	6.5686E-03
387	846	436	8.2257	1.1844E-01	0.4133	0.5867	3.2756E-02	6.5513E-03
388	843	437	8.2020	1.1801E-01	0.4198	0.5802	3.2637E-02	6.5274E-03
389	841	438	8.1785	1.1746E-01	0.4263	0.5737	3.2485E-02	6.4971E-03
390	838	439	8.1551	1.1680E-01	0.4328	0.5672	3.2301E-02	6.4603E-03
391	836	440	8.1318	1.1601E-01	0.4392	0.5608	3.2085E-02	6.4169E-03
392	834	441	8.1087	1.1511E-01	0.4456	0.5544	3.1836E-02	6.3671E-03
393	831	442	8.0857	1.1409E-01	0.4520	0.5480	3.1554E-02	6.3108E-03
394	829	443	8.0630	1.1296E-01	0.4583	0.5417	3.1240E-02	6.2480E-03
401	814	450	7.9121	1.0173E-01	0.5000	0.5000	2.8134E-02	5.6268E-03
411	794	460	7.7271	8.4030E-02	0.5511	0.4489	2.3239E-02	4.6479E-03
416	786	465	7.6467	7.7019E-02	0.5734	0.4266	2.1300E-02	4.2601E-03 *
421	779	470	7.5727	7.1234E-02	0.5939	0.4061	1.9700E-02	3.9401E-03
711	647	760	6.2998	9.8584E-03	0.9487	0.0513	2.7265E-03	5.4529E-04
718	645	767	6.2757	1.0137E-02	0.9526	0.0474	2.8036E-03	5.6072E-04*
721	645	770	6.2696	1.0082E-02	0.9542	0.0458	2.7883E-03	5.5766E-04
731	643	780	6.2502	9.1891E-03	0.9596	0.0404	2.5413E-03	5.0827E-04
741	641	790	6.2334	7.4762E-03	0.9643	0.0357	2.0676E-03	4.1352E-04
751	640	800	6.2208	4.9929E-03	0.9677	0.0323	1.3808E-03	2.7617E-04
761	639	810	6.2129	3.3151E-03	0.9699	0.0301	9.1683E-04	1.8337E-04
771	638	820	6.2060	4.0189E-03	0.9718	0.0282	1.1115E-03	2.2230E-04
781	637	830	6.1954	6.6452E-03	0.9748	0.0252	1.8378E-03	3.6756E-04
791	635	840	6.1801	8.4398E-03	0.9790	0.0210	2.3341E-03	4.6682E-04
800	634	849	6.1643	8.9512E-03	0.9834	0.0166	2.4756E-03	4.9511E-04*
801	634	850	6.1625	8.9435E-03	0.9839	0.0161	2.4734E-03	4.9468E-04
811	632	860	6.1451	8.3264E-03	0.9887	0.0113	2.3028E-03	4.6055E-04
821	630	870	6.1298	6.7586E-03	0.9929	0.0071	1.8692E-03	3.7383E-04
831	629	880	6.1186	4.5290E-03	0.9960	0.0040	1.2525E-03	2.5051E-04
841	628	890	6.1109	3.3718E-03	0.9981	0.0019	9.3251E-04	1.8650E-04
851	627	900	6.1042	3.5760E-03	1.0000	0.0000	9.8899E-04	1.9780E-04

Maximum Reaction Rate = 3.2920E-02 at α = 0.3936 at 433.0°C.
6 Reaction Rate Values between 423 and 443 °C are within 99.5% of the maximum.

increase in heating rate. It must be emphasized that the calculated DTG values are the correct ones.

Since for this particular coal there is an approximate 5% moisture loss, it

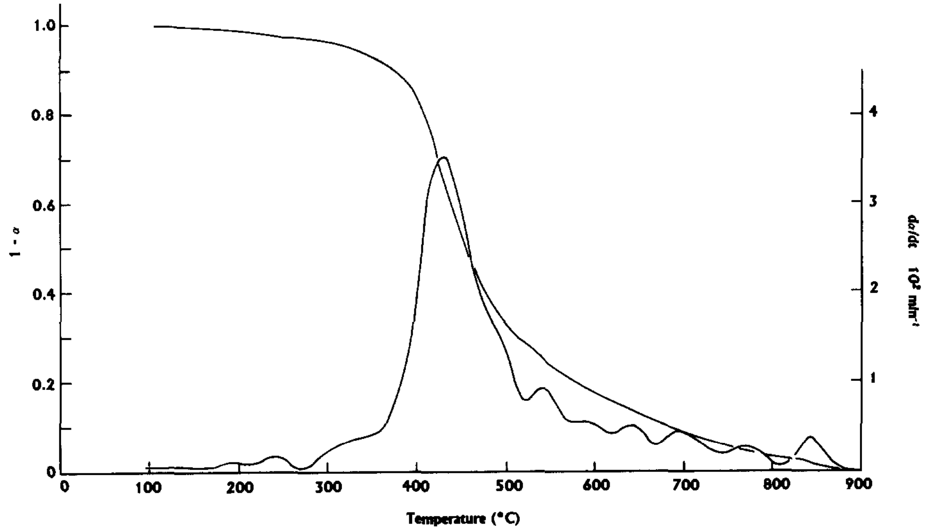

Fig. 4. The complement of the degree of reaction $(1-\alpha)$ and the rate of reaction $(\mathrm{d}\alpha/\mathrm{d}t)$ for the West-Kentucky #9 high volatile B bituminous coal at 5°C $\min^{-1}$.

is more correct to consider only those data obtained at and above 100°C. This has been achieved by a simple modification of the input (Tgin) data. Figure 4 shows the complement of the extent $(1-\alpha)$ and the rate of reaction $(\mathrm{d}\alpha/\mathrm{d}t)$ obtained by processing the modified data at 5°C $\min^{-1}$ in program TGDATCON. As can be seen, although there is a clearly defined "major loss of volatile material" region from ca. 350 to ca. 480°C, at $\alpha \approx 0.66$ other reactions start contributing to the overall weight-loss process. The nature of the physico-chemical processes possibly at work in this temperature region will be considered in a forthcoming paper. Suffice to say, as will be seen in part II, the region above $\alpha = 0.66$ is not truly amenable to kinetic analysis. However, within the main temperature region, 100–500°C, excellent reproducibility is obtained with these highly volatile bituminous coals, as shown in Fig. 5. Here, triplicate data obtained at a heating rate of 5°C $\min^{-1}$ lie within the envelope. Over the entire temperature range the extents of reaction as functions of temperature agree to within less than $\pm 1\%$. Similar precision is also obtained at other heating rates used, up to 150°C $\min^{-1}$. This augers well for an excellent kinetic analysis, as will be shown in part II.

ACKNOWLEDGMENT

This work was conducted as a part of the Kentucky Energy Resource Utilization Program supported by the Commonwealth of Kentucky, Kentucky Energy Cabinet.

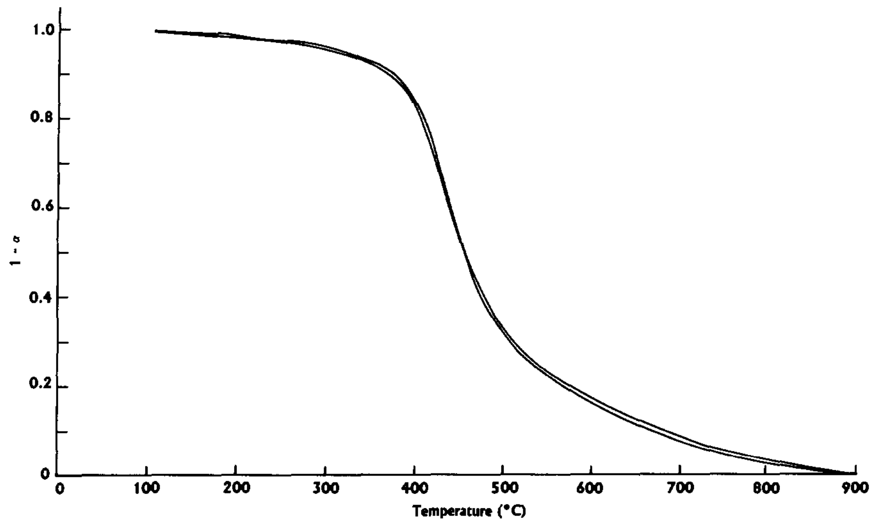

Fig. 5. Triplicate $1-\alpha$ data at $5°C\ min^{-1}$ for the West-Kentucky #9 high volatile B bituminous coal.

REFERENCES

1 J.P. Elder and M.B. Harris, Fuel, 63 (1984) 262.
2 J.P. Elder and V.B. Reddy, Proc. Eastern Oil Shale Symposium, Lexington, KY, 1983, p. 255.
3 J.P. Elder, J. Therm. Anal., 29 (1984) 1327.
4 C.F. Gerald, Applied Numerical Analysis, 2nd edn., Addison-Wesley, Reading, MA, 1977, Chap. 10.
5 S.D. Christian and E.E. Tucker, Am. Lab., 15 (1983) 35.
6 J.P. Elder, Thermochim. Acta, 52 (1982) 235.
7 C. Ridley, CUBSPL, National Center for Atmospheric Research, Boulder, CO 1978.
8 J.P. Elder, Proc. 7th ICTA, Kingston, Ontario, Canada, 1982, Wiley, New York, 1982, pap. V-C-5.