

DIFFERENTIAL SCANNING CALORIMETRY OF COAL

by

Phillip I. Gold

Department of Mechanical Engineering

California State University, Los Angeles

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1.0 Abstract

Differential Scanning Calorimetry studies performed during the first year of this project demonstrated the occurrence of exothermic reactions associated with the production of volatile matter in or near the plastic region.

The temperature and magnitude of the exothermic peak was observed to be strongly affected by the heating rate, sample mass and, to a lesser extent, by sample particle size. Thermal properties also were found to be influenced by oxidation of the coal sample due to weathering effects.

2.0 Acknowledgements

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5.0 Program Objectives

The objective of this project was the application of experimental thermal analysis techniques of Differential Scanning Calorimetry to the study of the thermal properties of coal below temperatures of active decomposition. Particular emphasis was placed on temperatures within and below the plastic range of coal (390°C to 490°C).

6.0 Summary of Results

A detailed description of the results and conclusions derived from this research in the first year of effort is presented in Section 9. A brief summary of these results is outlined in this section.

A number of coal samples ranging in rank from Low-volatile Bituminous to Subbituminous were tested. Thermograms for these samples displayed the existence of a sometimes very substantial exothermic transition within the temperature range 400-500°C. Although the appearance and magnitude of this exotherm did not appear to correlate with rank, available data were suggestive of a relationship between the reported plastic range and temperature of the peak.

Various experimental parameters were found to strongly influence the temperature and magnitude of the exothermic peak. Peak amplitude was increased at higher heating rates, which also caused a shift of the exotherm to higher temperatures. Volatilization rates and plastic characteristics of coal exhibit a similar behavior.

Sample particle size was also found to affect the exotherm, with reduced peak sizes observed for smaller particle size samples at all heating rates. This effect was attributed to partial oxidation of the smaller particles.

Sample mass was also found to influence the appearance of exothermic peaks. The exotherm was observed to diminish proportionally with decreasing sample mass, only to disappear sharply at some small sample size, at all heating rates. Increase of instrument sensitivity confirmed the absence of any peak.

The combination of these factors seems to point to a relationship between the occurrence of the exothermic transition and the production of volatile matter. Although some apparent exceptions to this conclusion were observed, thermogravimetric analysis and volatile matter detection were not sufficiently precise to settle the question. This matter will be actively pursued during the second year of this effort.

Partial oxidation or weathering was found to materially affect the observed thermal transitions as did preheating of samples at temperatures at which devolatilization was substantial.

Finally, because of the absence of thermogravimetric data, no quantitative calorimetric analysis of the samples tested was attempted. A quantitative calorimetric analysis will be a major objective of the second year of this study, made possible by the recent acquisition of micro thermogravimetric instrumentation.

7.0 Background

Research is underway to develop screw extrusion as a means of continuous injection of coal into high pressure systems (1-4). Coal is extrudable only when it reaches a temperature which is associated with the onset of its plastic state in which it can be handled as a viscous fluid. This temperature varies from about 390°C to 490°C for most coals (5). Coal will not extrude below its plastic range, and it forms hard coke, which is not extrudable above this temperature range.

Problems which have been encountered in attempting to demonstrate the feasibility of this concept include coke clogging of the auger or barrel, premature coking, incomplete heat transfer through the coal mixture, and volatile matter buildup. Also, the well known dependence of the plastic properties and range upon the heating rate (5) has led to control problems during the extrusion process (2). The chemical and physical changes which take place when coal is subjected to the action of heat and pressure during the extrusion process must be established in order to develop appropriate extruder design criteria.

The attainment of conditions required to extrude coal requires the development of extruder design criteria which match the thermal characteristics of the coal. The thermal properties of major interest are:

- (1) The total enthalpy required to heat the coal to extrusion temperatures, including both specific heat effects and thermal transitions resulting from physical or chemical changes.
- (2) The thermal conductivity of coal through the plastic range.

Coals, because of their mode of genesis would be expected to be resistant to thermal changes below temperatures at which pyrolytic breakdown occurs. There has been very little experimental work regarding the thermal properties of coal for temperatures below 500°C. The development of coal extrusion requires detailed information, especially in the plastic region, where small thermal transitions could affect the plastic characteristics of the coal.

Only two direct methods are available for the study of thermal transitions in coal below temperatures of active decomposition. Differential Thermal Analysis (DTA) is widely used to detect phase and compositional changes in minerals. In the conventional DTA approach, the temperatures of the sample, and of a thermally inert reference material in the same thermal environment are programmed. The absorption or evolution of thermal energy by the sample causes its temperature to deviate from that of the reference. This difference is recorded as a function of program, or sample temperature, and produces a scan consisting of negative or positive peaks. These peaks indicate the existence of exothermal or endothermal changes at the corresponding temperatures.

Differential Scanning Calorimetry (DSC) operates in a different manner. In DSC, as the temperature is programmed, the sample and reference temperatures are continuously maintained at the same level. When the sample absorbs or evolves energy, the differential power required to maintain the sample and reference temperatures at the same level is recorded. Since power is energy per unit time, DSC records the rate of energy absorption as a function of sample temperature. Consequently a peak area represents the energy of the associated transition when DSC is used with a linear time base recorder. Although a relatively new technique, DSC has proved to be an important tool in a wide variety of applications involving the study of thermal transitions.

7.1 DTA Investigations

DTA data for coal were perhaps first obtained by Hollings and Cobb (6) using a nitrogen atmosphere and coke as the inert comparison material. Their experiments showed the production of volatile matter commencing at about 250°C. Between this temperature and 1100°C, they distinguished a number of stages during which exothermic reactions predominated:

Endothermic	250°C - 410°C
Exothermic	410°C - 470°C
Endothermic	470°C - 610°C
Exothermic	610°C - 800°C
Endothermic	800°C - 1100°C

Glass (7, 8) reported thermograms for American coals ranging in rank from peat to meta-anthracite and concluded that the thermal effects are mainly endothermic. He used a covered cell in which 500 mg of sample was heated at a rate of 10°C/minute from room temperature to 1000°C in an atmosphere of the products of decomposition. He was able to detect five distinct types of thermograms which depend upon the plasticity of the coal and the structural, physical and chemical changes due to increasing rank. These types of thermograms were correlated with rank boundaries as shown in Table 7-1.

Glass' meta-anthracite type thermogram was characterized by a single volatile loss endothermic peak between 725-735°C. The anthracite type showed a single volatile loss peak between 630-680°C. The existence of a single volatile loss peak for the three highest coal ranks correlated with the absence of plasticity.

Table 7-1
Relationships Between Rank, Thermogram Type, and Plasticity*

Rank	Thermogram Type	Plasticity
Meta-anthracite	Meta-anthracite	Nonplastic
Anthracite	Anthracite	
Semi-anthracite		
Low-volatile Bituminous Medium-volatile Bituminous	Low-volatile	Plastic
High-volatile Bituminous	High-volatile	
Subbituminous Lignite Peat	Subbituminous	Nonplastic

*From Glass (7).

The low-volatile thermogram was characterized by two endothermic volatile loss peaks. The lower temperature peak in the range 350°-550°C corresponds to the range of primary devolatilization in which compounds containing carbon, hydrogen, and oxygen are released from the coal mass. The higher temperature peak in the range 600°-700°C correlates with the region of secondary degasification in which mainly methane and hydrogen are removed. Glass related the presence of two principal volatilization peaks to plasticity evidenced in bituminous coals.

The high-volatile type thermogram exhibited only by high-volatile bituminous coals was characterized by the appearance of a sharp exothermic reaction superimposed upon the endothermic primary volatilization peak. This produced two endothermic peaks at about 400°C and 500°C. Differences in the amplitude of the endothermic peaks distinguished HV A, B, and C coals.

The subbituminous type curve displayed a large primary volatilization peak at about 450°C. The secondary volatilization peak showed weakly between 500°-600°C when it was observed. Glass characterized this type of thermogram as representative of the nonplastic low-rank coals.

Examples of Glass' thermogram types are depicted in Figure 7-1. In addition to the characteristics described above, the thermograms exhibited a low-temperature endothermic devolatilization between 120°-150°C attributable to water loss or dehydration.

Glass also interpreted these curves as indicating the presence of small exotherms, one following the water loss endotherm and the other following the secondary volatilization endotherm at about 800°C. These features were not sharply defined as is the exotherm displayed by the high-volatile bituminous coals described above. They were more likely due to the return of the thermal curve to the baseline following relatively sharp endotherms and baseline drift effect (9).

Glass attempted to relate the behavior of the high-volatile type thermogram to the plastic properties of coals studied. Thermograms were compared with Giesler maximum fluidity and resolidification. He concluded that the coal is softening during the primary volatilization and selected the commencement of the observed exotherm as very nearly corresponding to the temperature for Giesler maximum fluidity. The point at which the primary endothermic effect becomes more pronounced than the neutralizing exothermic effect was designated as the resolidification point.

Although Glass refrained from speculating on the cause of this exothermic reaction, Van Krevelen (9) in analyzing Glass' data concluded that it was caused by the condensation of aromatic structures associated with the resolidification process. This explanation of the effect seems somewhat at variance with Glass' observed peak temperatures and reported resolidification point temperatures.

Whitehead et. al. (10-13) employed vacuum DTA on various coal types ranging from peat to a Pennsylvania low-volatile coal. Samples of 25 mg to 100 mg of material ground to pass 200 mesh were heated at a constant rate of 20°C/min to 1000°C, under a vacuum. Contrary to Glass' findings, these studies characterized the pyrolysis of coal as an essentially exothermic process. Thermograms gave evidence of exothermic peaks commencing with peat having a maxima around 300°C. This peak was shifted to higher temperatures with materials of higher rank as shown in Table 7-2.

Berkowitz (14) confirmed the predominant exothermic character of the pyrolysis of coals heated in a current of nitrogen up to about 550°C. 100 mg samples ground to pass a 60 mesh screen were heated at a constant rate of 6°C/min. In this study, all the coals ranging from a lignite to a low volatile bituminous coal, gave evidence of several exothermic reactions below 400°C and at least one in the range of 400°-500°C.

Both Whitehead and Berkowitz concluded that their thermograms could not be interpreted or correlated in terms of coal type or rank.

Figure 7-1
Glass (7)
DTA Thermograms

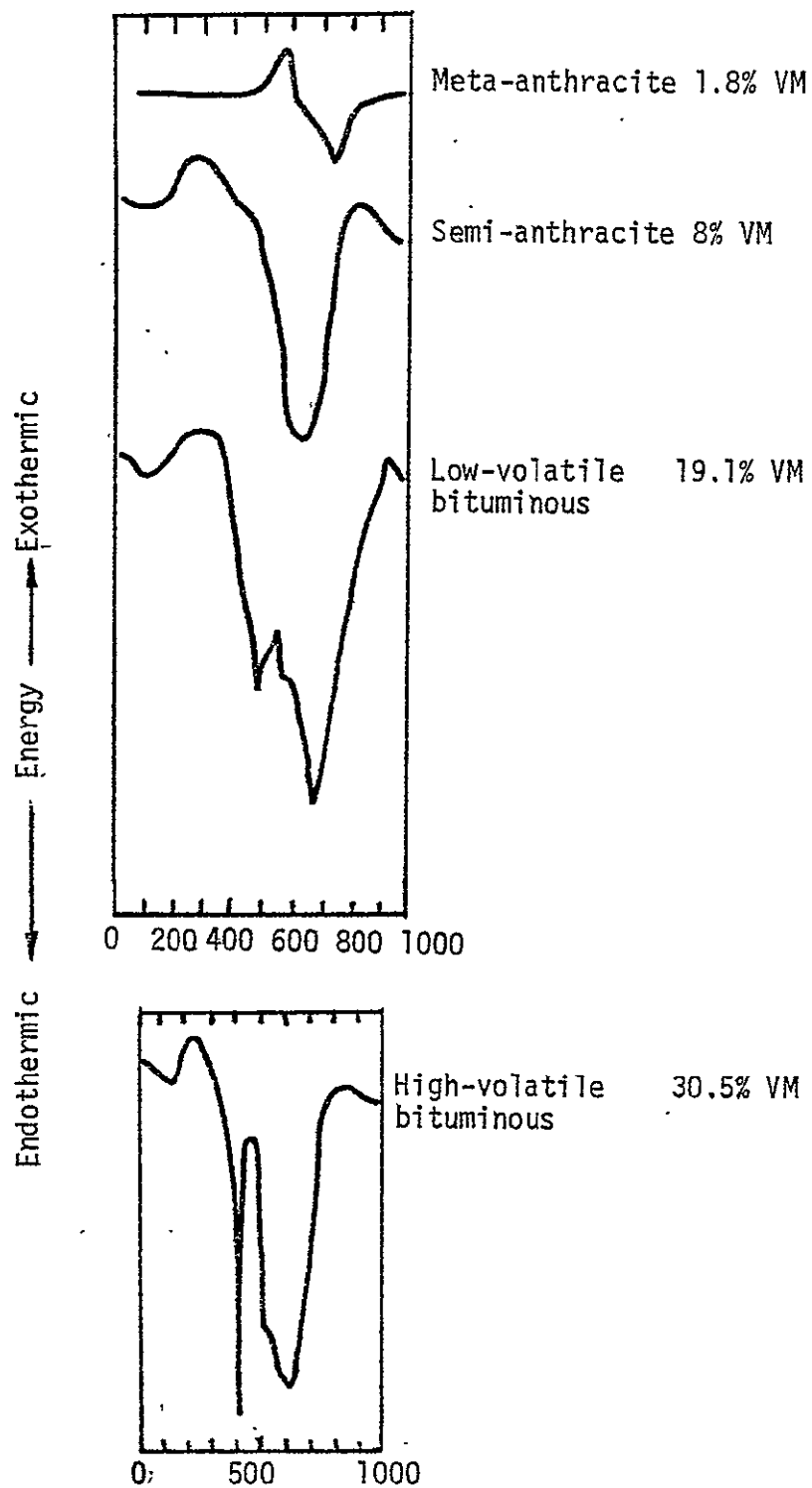


Table 7-2
Exothermic Peak Temperatures*

Rank	Approximate Exothermic Peak Temperature (°C)
Peat	300
Lignite	400-450
Subbituminous	
High-volatile Bituminous	450-500
Medium-volatile Bituminous	
Low-volatile Bituminous	525 (1 sample only)
Semi-anthracite	500 (1 sample only)
Anthracite	no peaks below 600°C

A number of other efforts have been made to resolve whether coal pyrolysis is endothermic or exothermic. Clegg (15) obtained sharp endothermic reactions using covered sample holders in an atmosphere of pyrolysis products in agreement with Glass.

Gains and Partington (16) using covered sample holders found coal pyrolysis to be endothermic to 650°C. However, after correcting for the effects of heat transfer and the latent heat of volatilization, they concluded that reactions between 400°C and 500°C were exothermic.

Pampuch and Roga (17) also agreed with Glass. They concluded that when coals of various ranks were pyrolyzed, the release of moisture (90°-120°C), the softening and release of volatile matter (320°-420°C) and the release of hydrogen (670°C-720°C) were all endothermic, while the solidification of the plastic mass (480°-540°C) was the only exothermic process. Kroger and Pohl (18) reached the same conclusions, i.e., that all reactions are endothermic, except the reactions between 440° and 550°C, which they ascribed to the solidification process. Boyer and Payen (19) suggested that this exothermic reaction is influenced by the rapid increase in thermal conductivity when the grains of the coal become agglutinated.

*From Breger and Whitehead (11).

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Kessler and Ramovackova (20) and Stephens (21) also contributed DTA studies of coal pyrolysis without resolving the question of the predominance of endothermic or exothermic processes.

The discrepancies between the various results described above are striking. The essential thermal character is either endothermic or exothermic. Thermograms either are or are not reliable predictors of rank or coking ability. The differences may be partly due to influences of the experimental methods employed. Individual thermograms of any particular material depend upon particle and sample size, heating rates, packing density, instrument sensitivity, and sample holder geometry. In addition, differences in the type of DTA technique used, i.e., vacuum, inert gas, or heating in an atmosphere of pyrolysis products could influence the result (9, 14). Masking of competing reactions or telescoping of reactions are substantially pronounced at higher heating rates (14).

Smith and Johnson (22) considered a number of problems inherent to thermal analysis of natural fuels, which could materially influence the character of the thermograms obtained. Of special interest is the effect of oxidation of the coal sample. Coal "weathering" during storage is a well-known phenomenon and has been shown to materially affect thermogram peaks (7). More striking perhaps is the surprisingly efficient combustion of coal even in trace amounts of oxygen. Combustion of coal in traces of air entering the DTA sample holder was one explanation advanced to account for the exotherm-endotherm controversy.

Other experimental difficulties inherent to natural fuels discussed by Smith and Johnson were: recondensation of oils or tars produced during pyrolysis, changes in thermophysical properties including heat transfer, heterogeneity of natural fuels, and large sample sizes required to avoid variations due to heterogeneity.

7.2 DSC Investigations

There have been relatively few applications of DSC to the study of coal pyrolysis due to its relatively recent development. Recently, Mahajan, et. al. (23) reported DSC thermograms for twelve U.S. Coals of various ranks in a helium atmosphere at 5.6 MPa (gauge) and temperatures up to 580°C. Using about 20 mg of dried sample at a heating rate of 10°C/min. they concluded the thermal effects during pyrolysis of coals ranging in rank from anthracite to HVC bituminous to be endothermic. Exothermic heats were observed only in the case of sub-bituminous or lignite coals. The net thermal effect was found to be strongly rank dependent. This work was unique in that an effort was made to correct the raw thermograms for the effect of volatile weight loss using the results of concurrent thermogravimetric analysis (TGA) of the samples tested. These corrections proved to cause a significant

change in the shape of the thermograms, in some cases leading to at least a partial reversal of the thermal effects.

Some very recent DSC and TGA scans were reported for samples of an HVB bituminous coal (4). These data show low temperature endothermic reactions at about 260° and 410°C and an endothermic reaction at 490°C. The low temperature endotherm was interpreted as a drying curve. The exotherm was observed to be highly dependent on heating rate, being only one-sixth as large when the heating rate was lowered from 100°C/Minute to 20°C/Minute.

7.3 Coal Weathering

It is well known that nearly all coals, when in contact with the atmosphere sooner or later show signs of weathering, as a result of which calorific values and coking properties are adversely affected. Even more significant is the fact that many coals in storage are liable to spontaneous combustion. This occurs when the heat evolved by oxidation cannot be dissipated.

Studies of the oxidation of coal by molecular oxygen may be classified as follows (7):

- (1) Studies of the chemistry of the oxidation process;
- (2) Determination of the reactivity of coal towards oxygen by empirical means;
- (3) Fundamental studies of the reaction kinetics of the oxidative process.

Studies of the chemistry of the oxidative process have been conducted utilizing microscopic examination, elemental analysis, thermogravimetric analysis, and chemical analysis of oxidation products. It has been found that oxygen is capable of penetrating very rapidly into the microscopic cracks present in coal. In addition, it appears that the oxidation process itself is composed of several stages which partly overlap one another as shown in Figure 7-2.

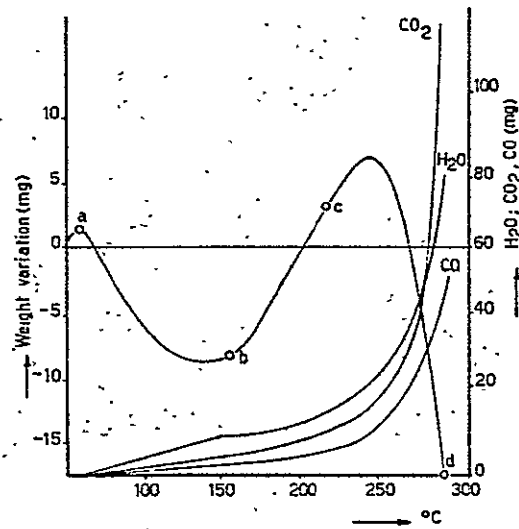
In the first stage (up to about 70°C) oxygen is taken up, probably by chemisorption, and the coal increases in weight. The weight decreases during the second stage as the adsorption complexes are broken down. Oxygen is also given off as oxides of carbon and through the release of intrinsic water (between 100°C and 150°C) during this second stage. The weight loss during the second stage exceeds the increase during the first.

The third stage (about 150°C-230°C) commences after the sample weight curve passes through a minimum. A sharp increase in weight is observed, which is accompanied by the formation of stable oxygen complexes and the evolution of heat.

Further increase in temperature leads to the fourth stage of oxidation (combustion) which is characterized by a sharp decrease in weight.

Figure 7-2

Weight Variation of Coal During Oxidation.
Van Krevelen (9).



Empirical determinations of the reactivity of coal toward oxygen center about the measurement of the ignition temperatures and initial temperature. Since neither of these temperatures is a physical constant, they must be obtained under strictly controlled standardized conditions (7).

Studies of reaction kinetics are based upon the observations of a specific physical parameter as a function of time and temperature. The following parameters have been used in kinetic studies of coal oxidation (7): weight, heat evolution, oxygen consumption, concentration of bound oxygen, character of gaseous reaction products, and others. Effects of partial pressure of oxygen, gas velocity, and particle size (specific outer surface area) have been observed.

Glass investigated weathering effects on the DTA thermograms of a number of coal types (7). He found these effects to increase with decreasing rank reaching a maximum in the plastic HVC coals. Thermograms of coals higher in rank exhibited only small changes.

Starting with an HVC coal which had been protected from exposure to air since the time of sampling, and powdering it to pass 60 mesh, Glass obtained thermograms on 15 successive days during which time the coal was exposed to air. These thermograms demonstrated a progressive change in the thermal curve except during the first day, when a sudden change took place. The changes occurred principally in volatile loss endotherms around 500°C and above, with very little effect on low temperature endotherms or the plastic-range exotherm.

7.4 Background Summary

The investigations described in the preceding two sections provide ample evidence of the existence of substantial exothermic processes above 400°C during coal pyrolysis. The temperature and magnitude of these processes, particularly in relation to any accompanying endothermic reactions are particularly dependent upon heating rate and whether the sample is heated in its own pyrolysis gases, an inert diluent, or a vacuum.

The mechanism by which the exothermic peak is produced remains unclear. If, as suggested by Van Krevelen (9), the exothermic peak results from resolidification of the plastic coal mass, the location of the peak should correlate with the resolidification temperature θ_s . On the other hand, pyrolysis produces a substantial mass of volatile matter which is readily oxidized in the presence of very small quantities of oxygen (22). Such reactions could well be responsible for the exothermic peak. Whatever the actual mechanism, it is clear that the exotherm occurs within, or very near, the plastic region and is associated with the production of volatile matter preceding and accompanying the softening process.

8.0 Experimental Procedures - Differential Scanning Calorimetry

The operation of the Model DSC-1B Differential Scanning Calorimeter is based on the temperature control of two similar sample holders in the sample holder assembly. The system consists of two separate "control loops", one for average temperature control, the second for differential temperature control.

In the average temperature loop, a programmer provides an electrical signal which is proportional to the desired temperature of the sample and reference holders. The programmer temperature information is relayed to the recorder temperature marker pen and appears as the abscissa scale marking. The programmer signal is compared with the average signal from platinum resistance thermometers in the sample and reference holders. If the temperature called for by the programmer is greater than the average temperature of the sample reference holders, more power will be fed to the heaters of both sample holders. If the average temperature is higher than that demanded by the programmer, the power to both heaters will be decreased.

In the differential temperature control loop, signals representing the sample and reference temperatures, measured by the platinum thermometers, are fed to a circuit which determines whether the reference or sample temperature is greater. The differential temperature amplifier output will then proportion a small increment of power between the reference and sample heaters in such a way as to correct any temperature difference between them. This is done by increasing the power to one while decreasing the power to the other.

When a transition such as melting, boiling, dehydration, or crystallization occurs in the sample material, an endothermic or exothermic reaction takes place. The change in power required to maintain the sample holder at the same temperature as the reference holder (i. e. its programmed temperature) during the transition, is the differential power and is recorded as a peak. The chart abscissa indicates the transition temperature. The peak area indicates the total energy transfer to or from the sample, or the enthalpy change corresponding to the indicated transition.

The temperature of a transition is usually assumed to be that temperature at which the first evidence of the change appears. In the DSC-1B, this will be the point of first observable deflection from the previously apparent "baseline".

The peak maximum of the recording of a transition by the DSC-1B indicates the temperature and time at which the transition is proceeding at a maximum rate.

If high accuracy of temperature information is desired, the calorimeter can be calibrated at well known transition points of pure materials, such as the melting points of metals run at conditions

precisely identical to those of the projected analyses. See Section 8.2.

The measurement of the area under a peak is best taken by the use of a mechanical planimeter. In order to convert this area reading to enthalpy of transition an ordinate or power calibration is performed as described in Section 8.3.

8.1 Differential Temperature Calibration

This procedure should be performed whenever a new sample holder is used or when the operator wishes to check calibration. If a new sample holder assembly is being calibrated, DIFFERENTIAL TEMPERATURE and AVERAGE TEMPERATURE controls should be initially set at 500. Adjust slope as required. The baseline can be centered with the ZERO control, if needed.

Place a standard calibration sample (e.g. indium) in each sample holder. Make sure the sample pan bottom is flat. Set the RANGE control at 16 and set the SCAN SPEED control at 10°/min. Scan through the sample melting point.

The right and left-hand peaks that occur when the temperature program passes through the melting point of the samples represent endotherms in the sample and reference pans, respectively.

If the sample pan endotherm occurred first, turn the DIFFERENTIAL TEMPERATURE CALIBRATION control CW. One turn of this ten-turn potentiometer will effect a change in the separation of the two endotherms of approximately 10°C. Repeat the entire procedure until both endotherms occur at the sample temperature, as indicated by a single peak.

This differential temperature calibration should be optimized over the temperature range of interest. If more than one calibration point is used, it may not be possible to achieve complete cancellation at every point.

8.2 Abscissa or Temperature Calibration

The abscissa or temperature error on the DSC-1B is 7°C max. over the upper temperature range and 15°C max. over the lower temperature range. Perfect accuracy is precluded by inherent non-linearities in the platinum sensors and other parts of the system. Although some of these non-linearities tend to cancel each other, the net output characteristic is non-linear.

Note that the indicated temperature is correct at two points. The DSC-1B temperature scale is factory-calibrated at a scan speed of 10° per minute at two points corresponding to the melting points of indium and lead, 429°K and 600°K, respectively, for the upper temperature range, and at two points corresponding to the melting points of n-octane and tin, 216°K and 505°K, respectively, for the

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lower temperature range. Calibration by means of melting points 100° apart will provide increased accuracy over a range extending from 50° below the low point to 50° above the high point.

Note: For greatest accuracy, temperature calibration should be made at the scan speed to be used. The indicated transition temperature will be higher than the true transition temperature at scan speeds higher than the calibration scan speed and lower at lower scan speeds. This effect is particularly noticeable at scan speeds of 40°/min. and 80°/min., where the deviation may be as much as 6°. At all other scan speeds the deviation is less than 2°. The adjustment of the indicated temperature can be made rapidly by means of the AVERAGE TEMPERATURE CALIBRATION control as described below.

Temperature calibration is performed as follows:

Place a calibration sample pan in the right-hand sample holder and the reference pan, R, in the left-hand sample holder.

Note: Metal samples should always be used in an aluminum pan, never directly on the sample holder.

Perform upper range calibration as follows (for lower temperature range substitute n-octane for indium): Make a run with an indium sample; program 10°/min. or at the scan-speed of interest and set RANGE at 16. Run until melting point is observed, note the temperature, then program down through the freezing point to about 400°K. The melting point is defined as the point of departure from the baseline. Replace the indium with a tin sample. Program up through the melting point, note the temperature, and program down until the freezing point is observed. Repeat this procedure with lead sample.

If the indicated lowest (indium) and highest (lead) melting points are displaced from their actual values of 429° and 600°K, respectively, by more than two degrees, calibration is required.

If both melting points are low, turn the AVERAGE TEMPERATURE CALIBRATION control clockwise. One full turn increases the temperature about 5°. If the indicated melting points are high, turn the AVERAGE TEMPERATURE CALIBRATION control counterclockwise. Recheck the melting points. Repeat this procedure if necessary.

8.3. Ordinate or Power Calibration

The positions on the RANGE switch on the front panel of the control unit indicate the nominal calibration, the maximum sensitivity being one millicalorie per second full scale, the next two millicalories per second full scale, etc. Full scale in this context means full 10-mv deflection of the recorder pen (from 0 to 100 on the chart paper).

To check the calibration or to recalibrate, establish a constant in terms of millicalories per square inch of chart as follows:

1. Compute the energy of transition (e.g., heat fusion) of a known weight of sample.
2. Run the sample through the transition at an appropriate scan speed, RANGE setting and chart speed (typically 100/min. X16 RANGE and 4 in/min. respectively) and measure the resulting area with a planimeter.
3. Compute the constant K_N as follows:

$$K_N (\text{MILLICALORIES/IN}^2) = \frac{\text{HEAT OF FUSION (MILLICAL/MG) X SAMPLE WEIGHT (MG)}}{\text{AREA UNDER PEAK (IN}^2\text{)}}$$

4. To determine transition enthalpies, multiply the measured peak area in square inches by the constant

$$K(H_X = K_N \times A_X).$$

If chart speeds and RANGE settings other than those used to determine K_N are used, the constant must be normalized

accordingly. For example, if a chart speed of 1 in/min. and a RANGE of X32 are used, the normalized constant

$$K_N' \text{ is } K_N \times \frac{4}{1} \times \frac{32}{16} = 8K_N.$$

The general normalizing relationship is thus:

$$K_N' = \frac{\text{NORMAL CHART SPEED}}{\text{NEW CHART SPEED}} \times \frac{\text{NEW RANGE SETTING}}{\text{NORMAL RANGE SETTING}} \times K_N$$

8.4 Slope Setting

Corrects slope of the baseline by adjusting the power applied to the heater of each sample holder. The control compensates for differences in heat dissipation characteristics of the sample holders. It is normally adjusted at the high end of the temperature range, where the greatest differences in these characteristics occur.

For greatest ordinate precision, calibration should be performed at the SLOPE setting to be used. Generally if the SLOPE control is varied by no more than one complete revolution CW or CCW from the value at which the ordinate calibration is performed, the calibration remains valid to $\pm 1\%$.

8.5 Sample Shape

The DSC-1B can analyze solid and liquid samples. Solid samples can be in foil, powder, crystal or granular form. Although quantitative accuracy will remain essentially the same regardless of sample shape, the qualitative appearance of the run will be affected by the sample configuration. Therefore, for maximum peak sharpness and resolution, a configuration which maximizes the contact surface between the pan and sample is desirable. Thin discs or films of sample or fine granules spread in a thin layer on the pan are the best shapes for optimum performance. Materials such as polymer films can be conveniently sampled by cutting out sections of the film with a standard paper punch or cork borer. Solid materials can be sliced into thin sections with a razor blade or knife.

8.6 Sample Weight

The proper weight of sample depends upon the problem but will ordinarily vary between 0.5 mg and 10 mg. Use small samples where the transition energy to be measured is very high; conversely, use large samples where low energy transitions, such as second-order glass transitions, are to be measured.

Small samples:

1. Permit higher scan speeds.
2. Yield maximum resolution, better qualitative results
3. Yield most regular peak shapes
4. Permit better sample contact with controlled atmospheres and better removal of decomposition products

Large samples:

1. Permit observation of small transitions
2. Yield more precise quantitative measurements
3. Produce larger quantities of volatile products for detection by the effluent analysis system

Solid samples can be easily handled as 40 mesh (or finer) powders or thin films, and as fibers. Except for polymers, samples occurring in chunk form either should be ground to 40 mesh powder or dissolved and left in a sample pan until the solvent has evaporated. Films can be cut to suitable size with a cork borer. Fiber samples should be cut into small pieces, if possible.

8.7 Effluent Analysis

The effluent analysis capability of the DSC-1B includes provision for detecting CO_2 , water vapor, and other decomposition products. The system includes a two-thermistor bridge, a detector block with by-pass valve, a detector block thermostat, a heated effluent line, and related controls. A potentiometric recorder and a carrier gas (nitrogen) complete the detection system.

The system can be tested and calibrated by injecting a known volume of water vapor, CO_2 , or other gas. The thermal conductivity type detector is particularly sensitive to contamination by condensible vapors in the effluent. The effect of contamination on detector performance is to substantially reduce detector sensitivity resulting in an uncertainty regarding the temperatures at which volatiles appear.

9.0 Results and Conclusions

9.1 General Characteristics of DSC Thermograms of Coal and Coal Chars.

DSC analyses of the coals studied were conducted according to the methods and procedures described in the previous section. Figure 9-1 depicts a typical sequence of scans which includes the instrument base-line and thermograms of the fresh coal sample as well as the low-temperature char for a high volatile bituminous coal (Utah A, PSOC-238). Low-temperature char thermograms were obtained by reheating the original sample after the initial scan to 500°C. The fresh sample and char thermograms, normalized for base-line shift are shown in Figure 9-2.

The general positive slope of the two normalized thermograms in Figure 9-2 results from a combination of sample weight loss and the temperature dependent specific heat. Although the effects cannot be separated unless the thermograms are corrected for weight loss, variation of the specific heat is the more important of the two. This conclusion follows the observation that the two thermograms have roughly the same overall slope, while the weight loss incurred by the reheated char was less than 10% of that observed for the fresh coal sample.

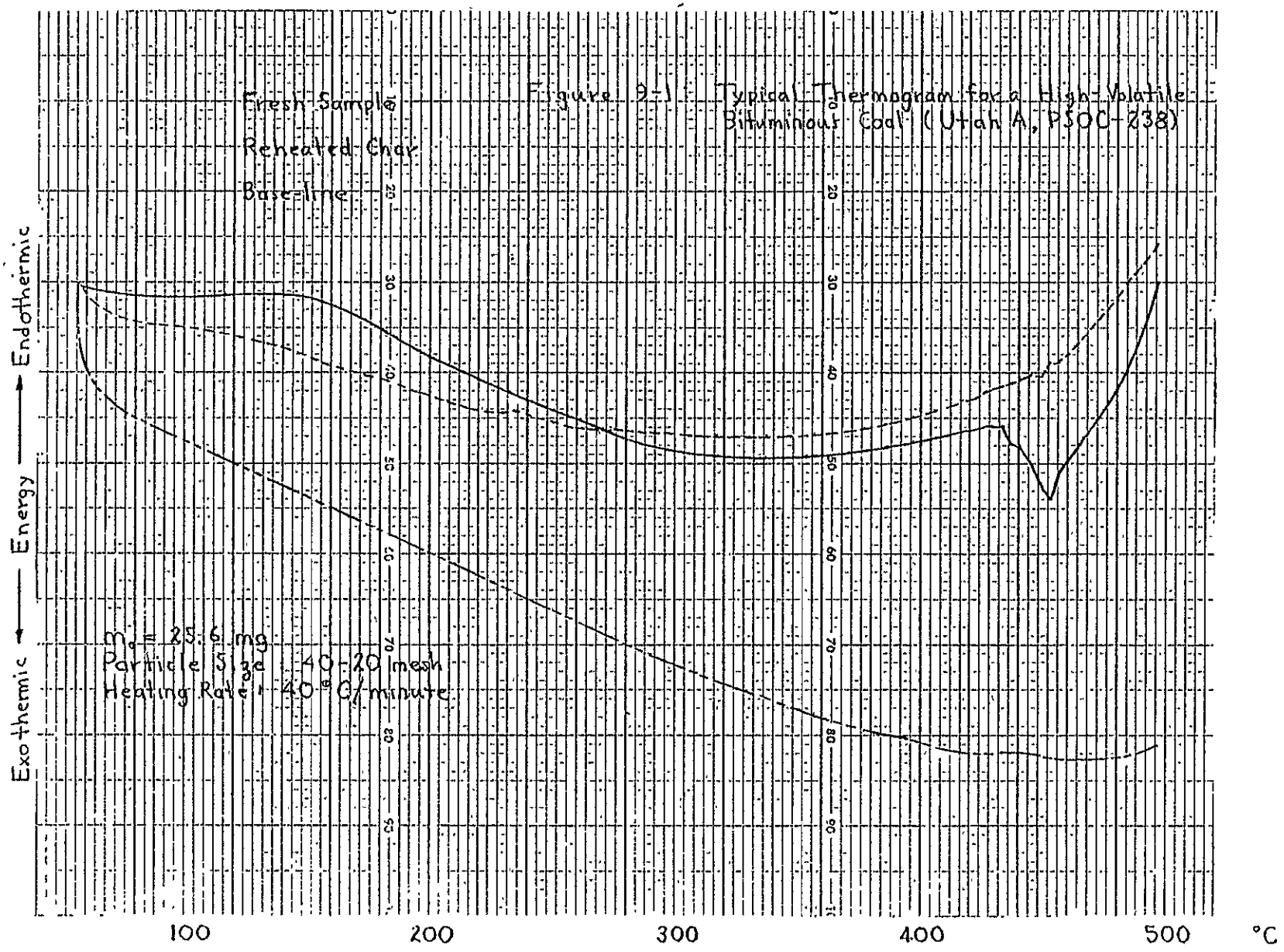
Thermal effects of chemical or physical transitions are characterized by positive (endothermic) or negative (exothermic) peaks. The broad endotherm observed peaking at about 150°C can most likely be attributed to the release of water since its amplitude correlates with the moisture content of the sample tested. The sharp exotherm commencing at about 430°C was preceded by the release of volatile organic matter observed at about 360°C and above.

9.2 Comparison of Coal Samples

A number of coal samples were selected for analysis. The selection was intended to be a representative one designed to highlight behavior in the plastic region. The coals chosen are listed in Table 9-1. The detailed characteristics of the thermograms of the coals listed do not differ in any of the essential elements from those shown in Figure 9-1.

Figure 9-3 depicts thermograms of various of the samples obtained under the conditions shown in the figure. These thermograms were obtained for purposes of comparing the behavior of the different samples, and no effort to adjust the instrument base-line was made. The salient features of qualitative note shown here are the low-temperature dehydration endotherm and the sometimes sharp exotherm just above 400°C. In the case of PSOC 238 and KY No. 9, the appearance of an endotherm following the exotherm just below 500°C is suggested. This observation is confirmed later.

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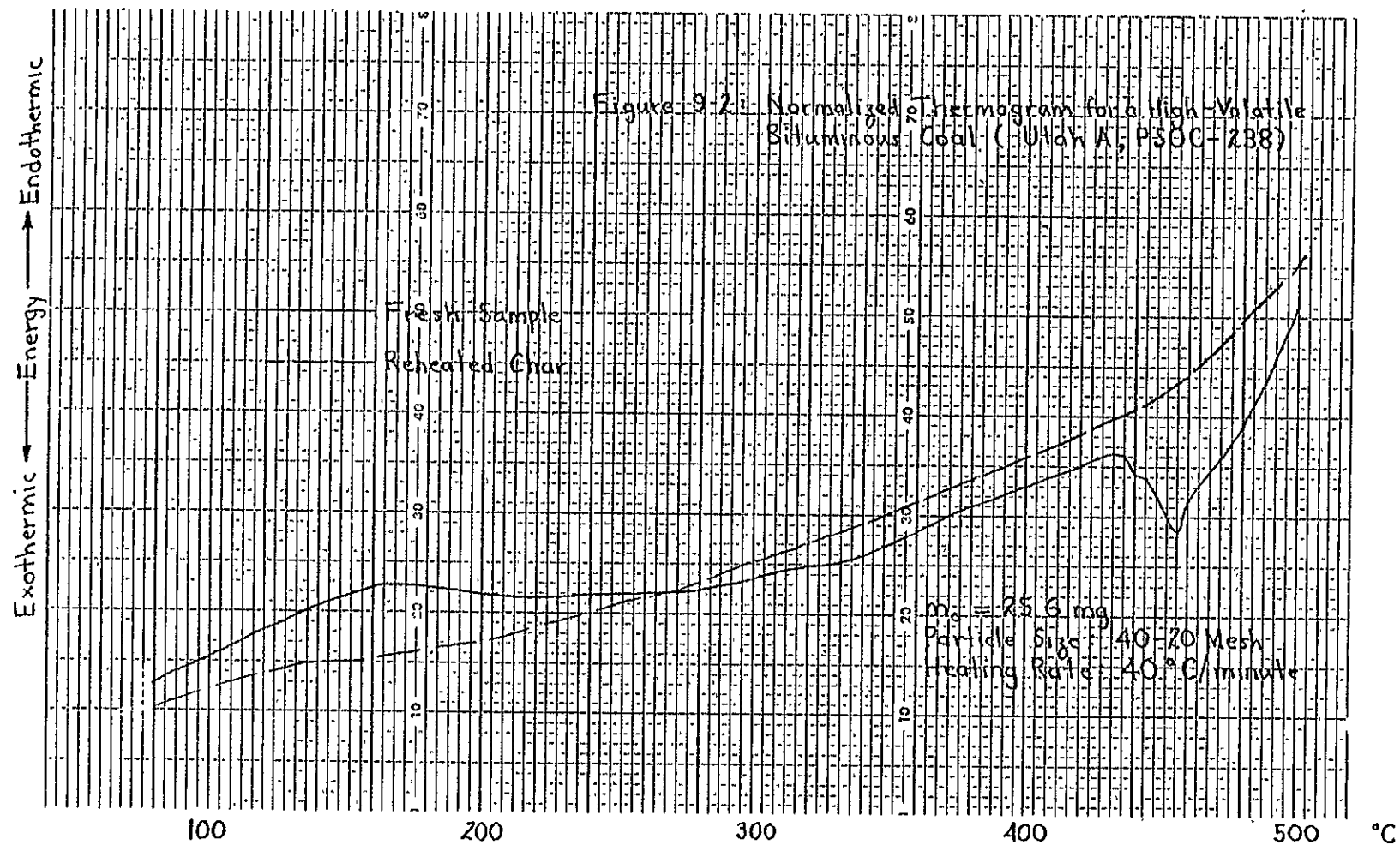


Table 9-1
Coal Samples Investigated⁺

Sample Identification		Mine Location	Rank	% Fixed C (DMMF)	% Volatiles (DMVF)	Calorific Value (MMMF) (Btu/lb)	% Moisture*	Softening Temperature (°C)	Max. Fluidity Temperature (°C)	Resolidification Temperature (°C)	Plastic Range (°C)
PSU No.	Seam or Mine										
1.	PSOC-233	Wadge	Colorado	HVC	58.20	41.80	12591	7.54			
2.	PSOC-238	Utah A	Utah	HVA	54.66	45.34	14018	3.60			
3.	PSOC-300	Pee Wee	Tennessee	HVA	61.12	38.88	14562	2.77	416	444	465
4.	PSOC-310	New Mexico #7	New Mexico	HVC	56.61	43.39	12208	11.07			
5.	PSOC-314	Blind Canyon	Utah	HVA	52.68	47.32	14004	4.08	408	432	456
6.	PSOC-316	Fish Creek	Colorado	HVC	59.38	40.62	12059	12.12			
7.	PSOC-318	Upper Freeport	Pennsylvania	Low Vol.	80.70	19.30	15278	2.93	471	498	508
8.	PSOC-336	Upper Freeport	Pennsylvania	Med. Vol.	74.12	25.88	14847	6.13	415	462	493
9.	PSOC-399	Fort Scott	Oklahoma	HVA	53.05	46.95	14492	3.99	378	450	479
10.	PSOC-414	Darco Lignite	Texas	Subbit C	50.53	49.47	8446	31.05			
11.	-	Orient #3, Ill #6	Illinois	HVC	55.9*	36.8*	10500-11500	1.4			
12.	-	Kentucky #9	Kentucky	HVR							

⁺All data (except for samples 11 and 12) were provided by the Pennsylvania State University Coal Research Section. Data for samples 11 and 12 were provided by Dr. Christopher England of JPL.

*As received.

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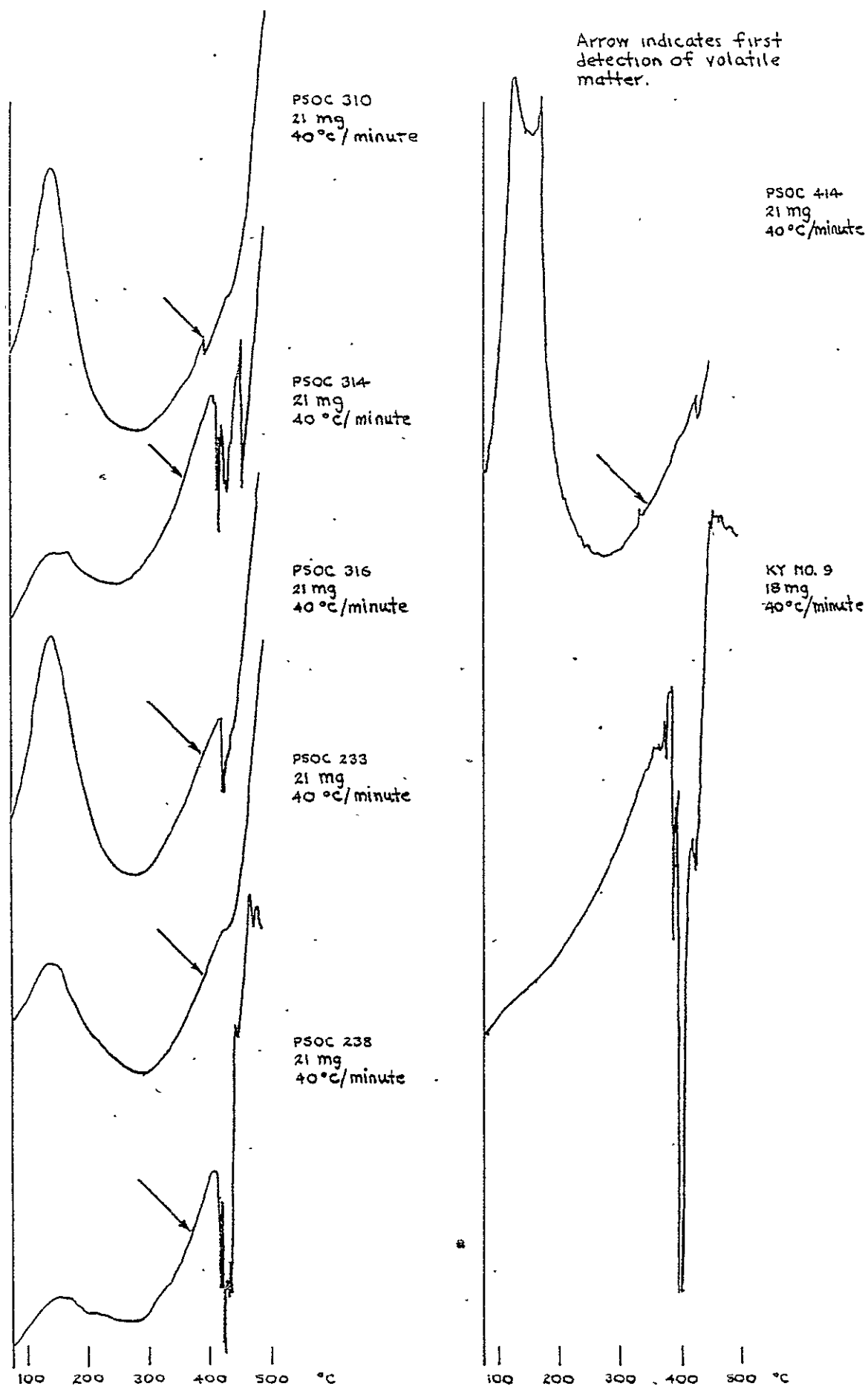


Figure 9-3: Comparison of Coal Samples.

A comparison of coal samples under instrumental conditions producing a relatively horizontal base-line in the temperature range of the expected exothermic peak (360° - 500°C) is shown in Figures 9-4 and 9-5. The highest accessible heating rate ($80^{\circ}\text{C}/\text{minute}$) was used in the cases depicted in Figure 9-4. The resulting exotherms are strikingly apparent. The onset of the exothermic process is characterized in these thermograms by a (relatively) sharp change of slope which occurred in the temperature range of 415°C - 475°C .

There appears to be no correlation between rank and the magnitude or location of the exotherm. However, when the available data are superimposed on the thermogram, the plastic range is seen to very nearly coincide with the exothermic peak. Although this observation is certainly suggestive, the effect of heating rate on both the plastic range and the location of the exotherm is not accounted for. Plastic range data were obtained from the PSU Coal Data Base which does not specify the heating rate used. The ASTM Standard Method of Test D1812-69 specifies a heating rate of $3^{\circ}\text{C}/\text{minute}$ which is the probable condition for the reported data. In any event, it is not likely the heating rate exceeded $10^{\circ}\text{C}/\text{minute}$ for the reported data, and the plastic properties would be expected to differ markedly at $80^{\circ}\text{C}/\text{minute}$. The very substantial influence of heating rate on the thermal transitions of coal will be described shortly.

In several of the cases depicted in Figure 9-4 (Ky No. 9, PSOC 238, and PSOC 310), an endotherm is observed immediately following the exotherm. It is apparent that this endotherm would have appeared in the remaining thermograms had the heating proceeded beyond the instrument limit of 500°C .

Figure 9-4 depicts two cases (PSOC 336 and PSOC 399) in which the exotherm appears to be interrupted by a sharp endotherm which gives way in turn to another exotherm. This type of behavior was observed periodically in the thermograms of samples exhibiting strong exotherms from a combination of the effect of temperature gradients within the sample, inhomogeneity of the sample, and splat-tering of material out of the sample holder. See also the PSOC 399 thermogram in Figure 9-5.

Finally, several of the thermograms (PSOC 336, PSOC 318, and others) indicate that the exotherm is preceded by the development of a relatively broad endotherm.

These observations are in agreement with those of Glass (7) that the exotherm itself is superimposed on a volatile matter endotherm, which commences at a somewhat lower temperature. It was the experience of this research, however, that volatilization, obtained independently of the calorimetric measurement, did not always precede the exotherm (see Figures 9-3 through 9-5). Rather, particularly at the highest heating rates, volatilization was not detected until well after the commencement of the exotherm. In addition, many samples exhibited substantial exotherms without generating any detectible volatile matter, while others generated volatile matter, but exhibited no exotherm.

Figure 9-4: Comparison of Coal Samples (20 mg, 80°C/min, 50-40 mesh)

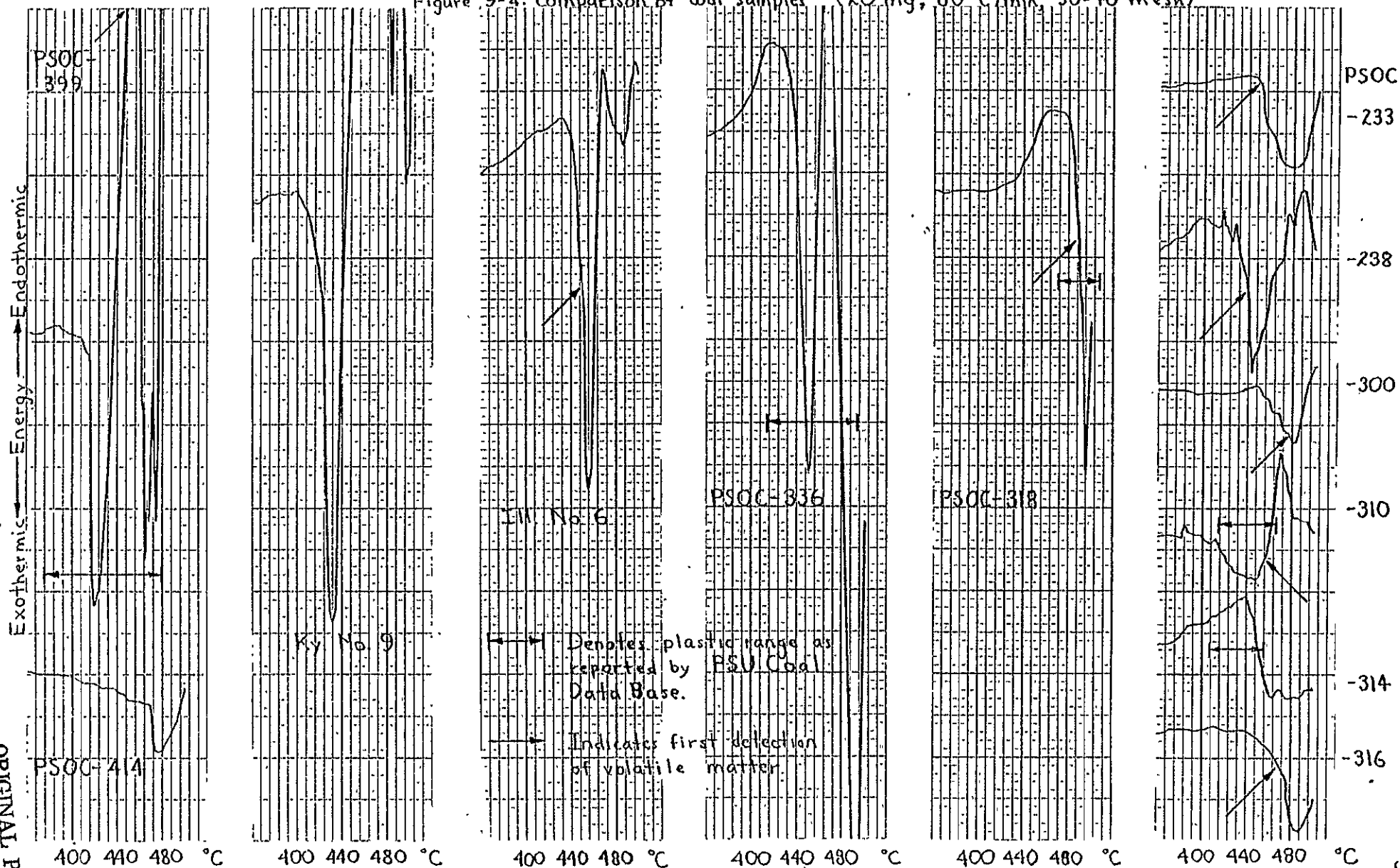
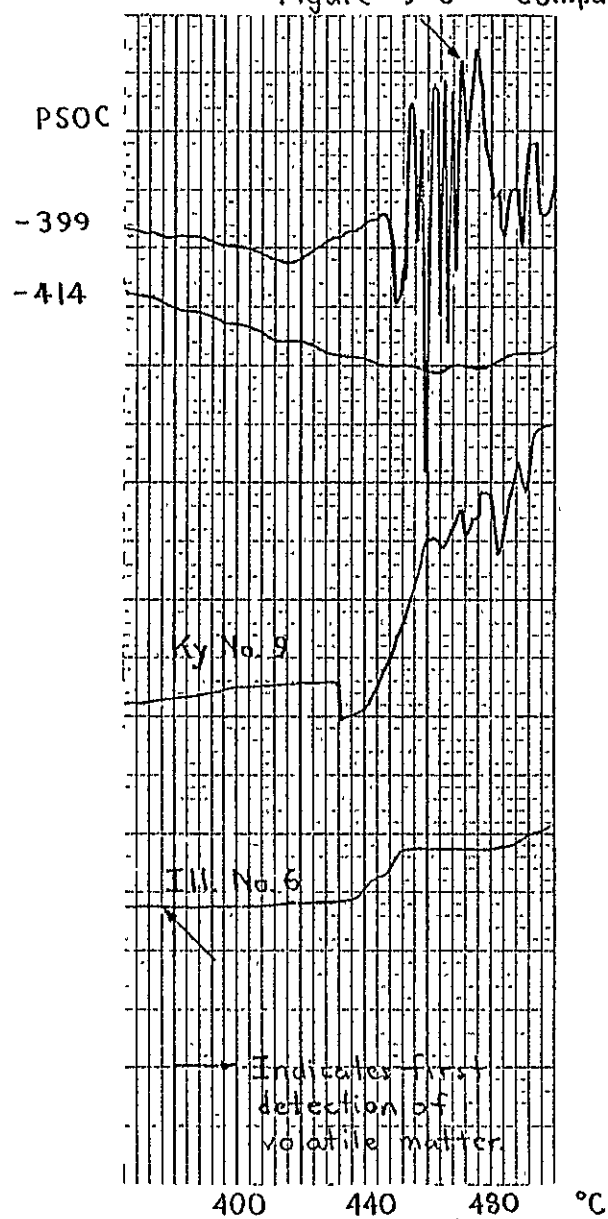
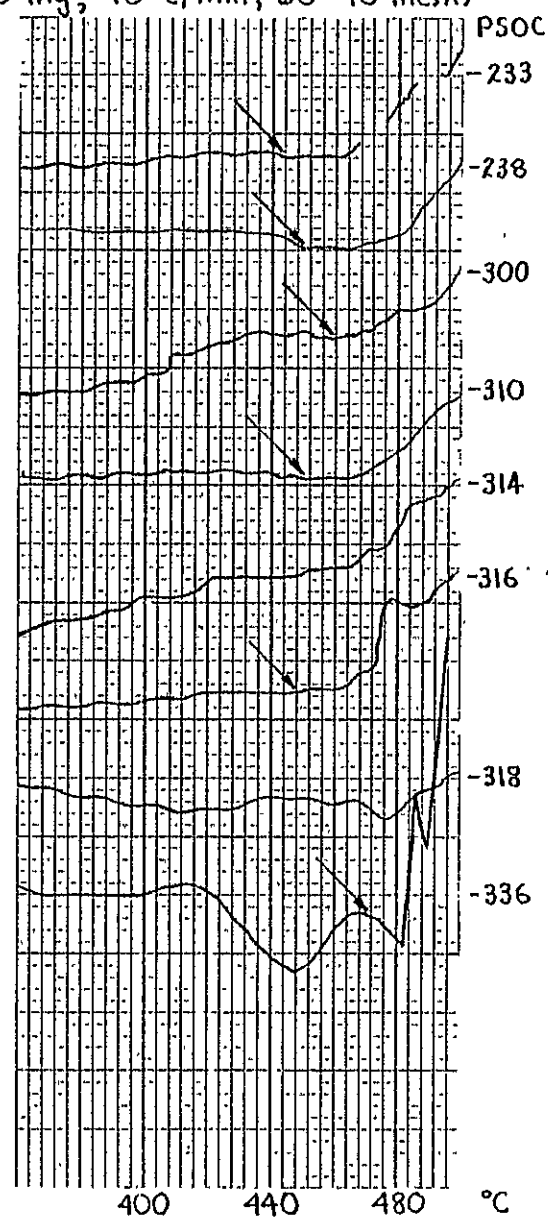


Figure 9-5: Comparison of Coal Samples (10 mg, 40°C/min, 50-40 mesh)



Exothermic ← Energy → Endothermic



Thus, although it seems reasonable to speculate whether the exotherm might not result from a vapor phase oxidation of the volatile products (22), such a conjecture appears inconsistent with the above observations.

9.3 Effect of System Operating Parameters

The controversy regarding the inherent endothermic or exothermic character of coal thermograms, and the possible role of the various experimental parameters was discussed in Section 7. Certain of these parameters were fixed very early in this work as a result of practical constraints imposed by the peculiar characteristics of coal.

Coal samples were placed in sample pans without compaction and covered with a loosely fitting sample pan holder. This arrangement was chosen to prevent splattering of the sample during heating while permitting the free escape of volatile matter into the blanketing inert gas stream.

Nitrogen gas was fed into the sample pan holder at the highest rate possible without disturbing the sample.

The remaining operational parameters investigated were heating rate, particle size distribution, and sample size. Table 9-2 outlines the experimental matrix performed to illustrate the effects of these parameters. Illinois No. 6 (HVC) was selected for this experiment.

The effect of heating rate on the magnitude and location of the exothermic peak is shown in Figures 9-6 and 9-7 for 30-20 mesh and 100-80 mesh samples, respectively. These thermograms clearly show the increased magnitude of the exothermic peak with increasing heating rate. The effect of particle size is also demonstrated by a comparison of the two figures. This effect will be discussed shortly, however, it is noteworthy to observe in Figure 9-7 that the exothermic reaction which occurred when the sample was heated at 80°C/minute is not present in the thermogram of the sample heated at 10°C/minute.

The thermograms obtained at 20°C/minute and 10°C/minute for 30-20 mesh coal depicted in Figure 9-6 exhibit erratic behavior caused by the apparent masking of competing exothermic and endothermic peaks. In view of the earlier explanation of this behavior observed in Figures 9-4 and 9-5, it seems surprising to note its absence at the higher heating rates. It is probable, however, that the effect was simply overwhelmed by the exothermic peak which was very substantial at the higher heating rates.

Figures 9-6 and 9-7 also reveal the effect of heating rate on the temperature at which the exothermic peak began, and the temperature at which volatiles were first detected. The volatilization temperatures and the peak temperatures depicted both shift to higher values at higher heating rates. This observation is consistent

Table 9-2
Experimental Matrix

Sample Weight (mg)	20				10			
Heating Rate ($^{\circ}\text{C}/\text{min}$)	80	40	20	10	80	40	20	10
Particle Size (mesh)								
20 - 10	x	x	x	x	x	x	x	(x)
30 - 20	x	x	x	x	x	x	(x)	(x)
40 - 30	x	x	x	x	x	x	x	(x)
50 - 40	x	x	x	x	x	(x)	(x)	
60 - 50	x	x	x	(x)	x	x	x	
80 - 60	x	x	x	(x)	x	(x)	(x)	
100 - 80	x	x	x		x	(x)	(x)	
-100	x	x	x		x	(x)		

Note: Where succeeding runs evidence no thermal reactions as indicated by the symbol (x), subsequent runs in the sequence were omitted.

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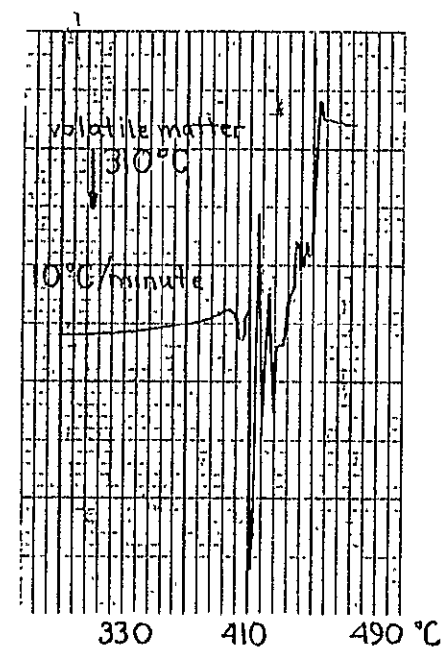
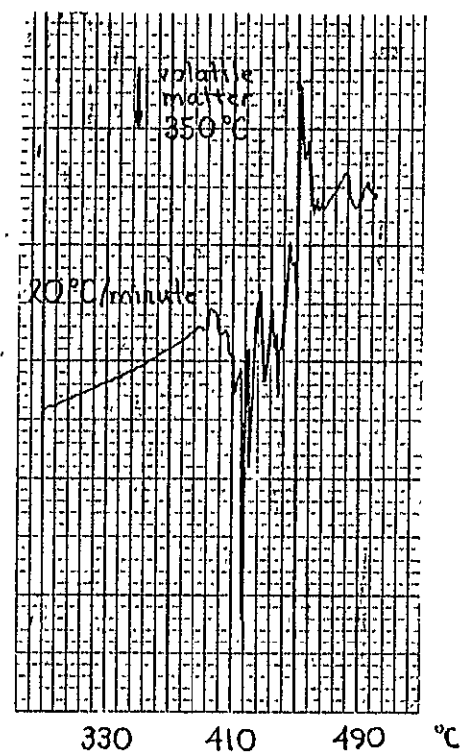
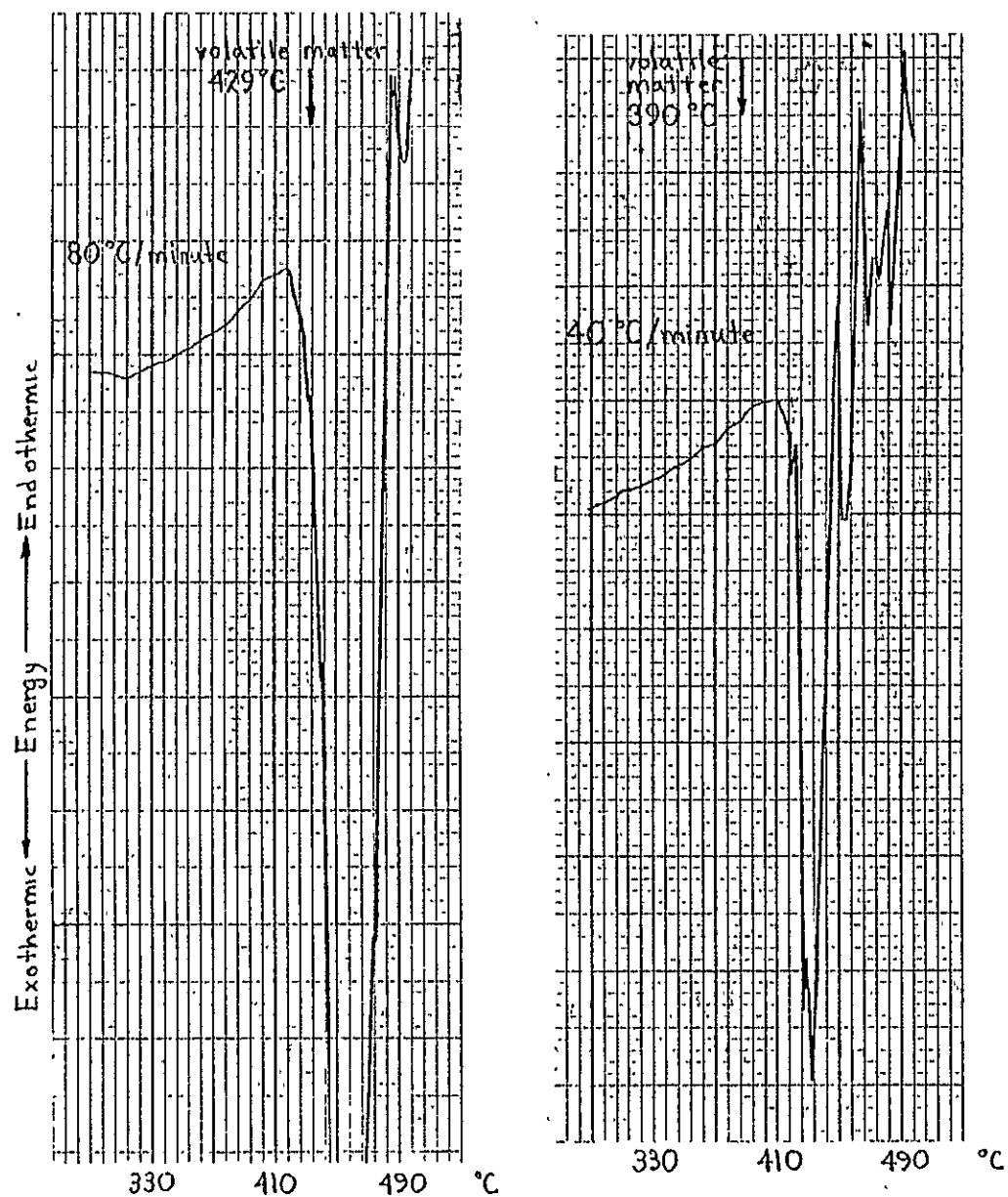


Figure 9-6: Effect of Heating Rate on DSC Thermogram.

III. No. 6 (HVC)
30-20 mesh
20 mg

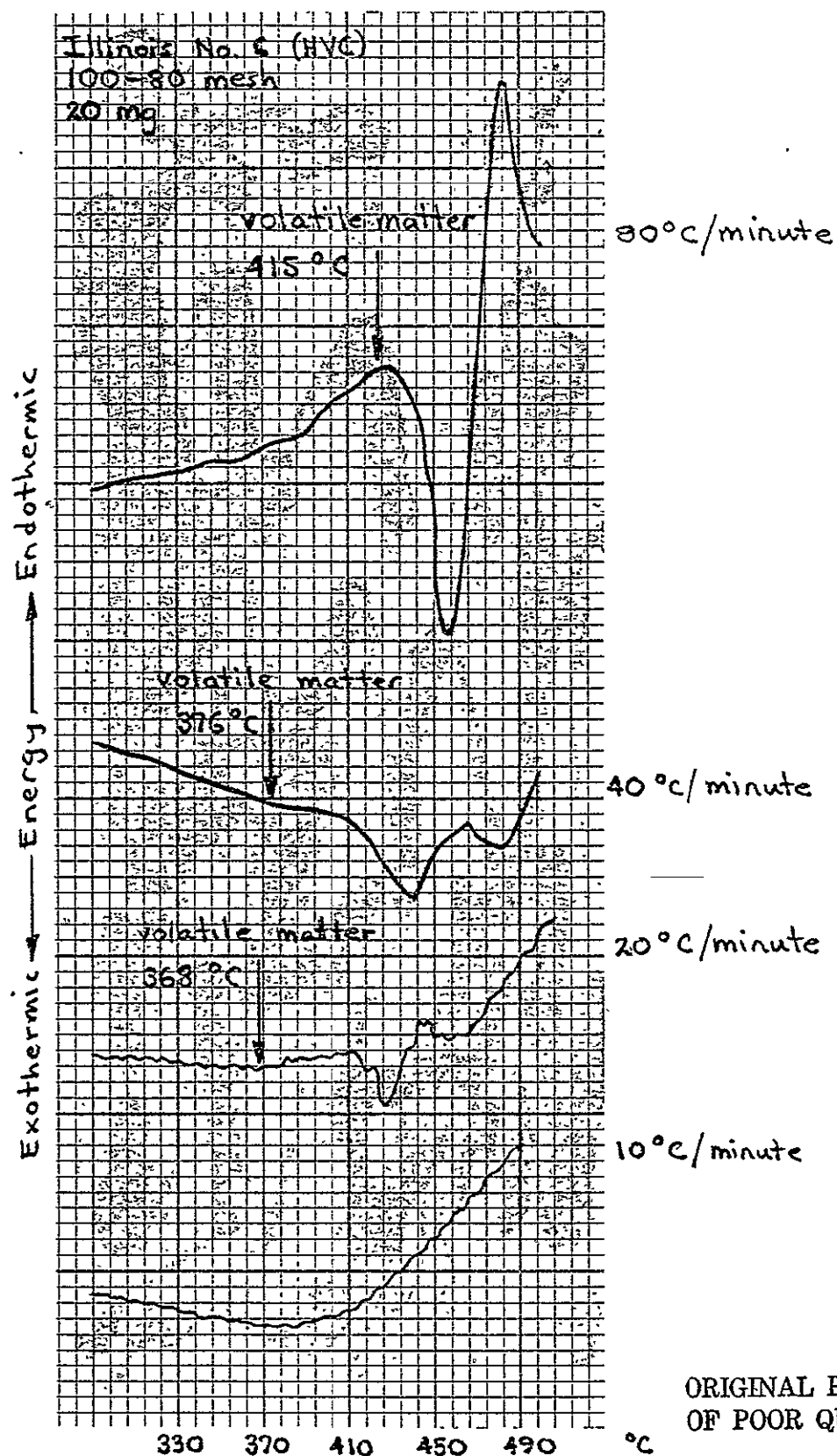


Figure 9-7: Effect of Heating Rate on DSC Thermogram.

with the reported behavior of the maximum devolatilization rate, temperature and magnitude of maximum plasticity, and dilatation, all of which experience a shift of the respective characteristic temperatures to higher values at higher heating rates (9).

Figures 9-6 and 9-7 indicate a greater shift of the detection temperature of volatiles than the peak temperatures. In Figure 9-6, for example, volatiles are shown at 310°C at a heating rate of 10°C/minute and 429°C at 80°C/minute. That is, volatiles were detected fully 100°C before the exotherm at 10°C/minute and 20°C after the start of the exotherm at 80°C/minute. Once again, the relationship of volatilization and the exothermic peak is brought into question by the overlap of the respective characteristic temperatures. The limitations of the volatile matter detector described in Section 8 cast some doubt on the results obtained at higher heating rates. It remains for a more thorough thermogravimetric analysis to settle this question.

A comparison of the thermograms depicted in Figures 9-6 and 9-7 depicts the effect of heating rates on samples of 30-20 mesh and 100-80 mesh coal. As illustrated, the peaks were substantially reduced for the smaller particle-size sample at all heating rates. Figure 9-8 shows this effect directly for samples over a range of particle-sizes at a heating rate of 80°C/minute. Here the effect on peak size is seen to be concentrated at the higher end of the particle-size spectrum.

Partial oxidation or weathering of the coal samples is the likely cause of this decrease in peak size. Coal is readily oxidized in air (9,22), and the extent of oxidation would be greater for the smaller particles due to the increased surface area. As seen in Figure 9-8, samples passing through a 100 mesh screen exhibited no exothermic peak.

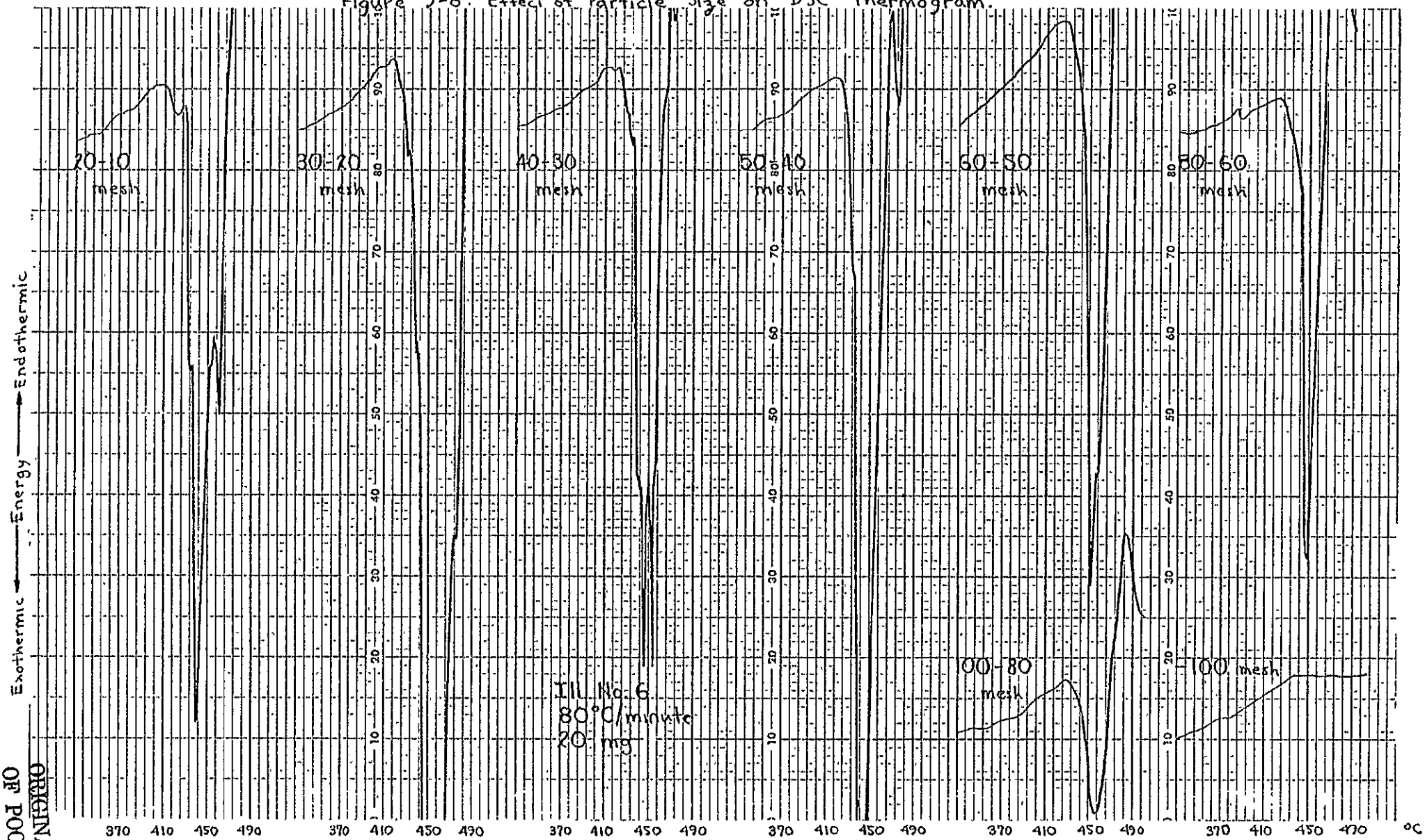
Sample size is also an important parameter in thermal analysis. Several factors influencing the choice of sample size are:

- a. The possibility of temperature gradients existing within larger samples especially at higher heating rates.
- b. Inhomogeneity of coal.
- c. Splattering of material out of the sample pan as volatile matter is released.

Thus, a sample size must be chosen so as to avoid spurious results due to such factors.

Experience with the DSC analyses of coal samples during this research indicated a more fundamental relationship of sample size to the appearance of exothermic peaks. This relationship is

Figure 9-8: Effect of Particle Size on DSC Thermogram.



illustrated in Figure 9-9, wherein the magnitude of the exothermic peak is a strong function of sample size. This is to be expected, however, data not shown in the figure indicate that the continuous decrease in magnitude with decreasing sample mass lead eventually to an abrupt disappearance of the exotherm.

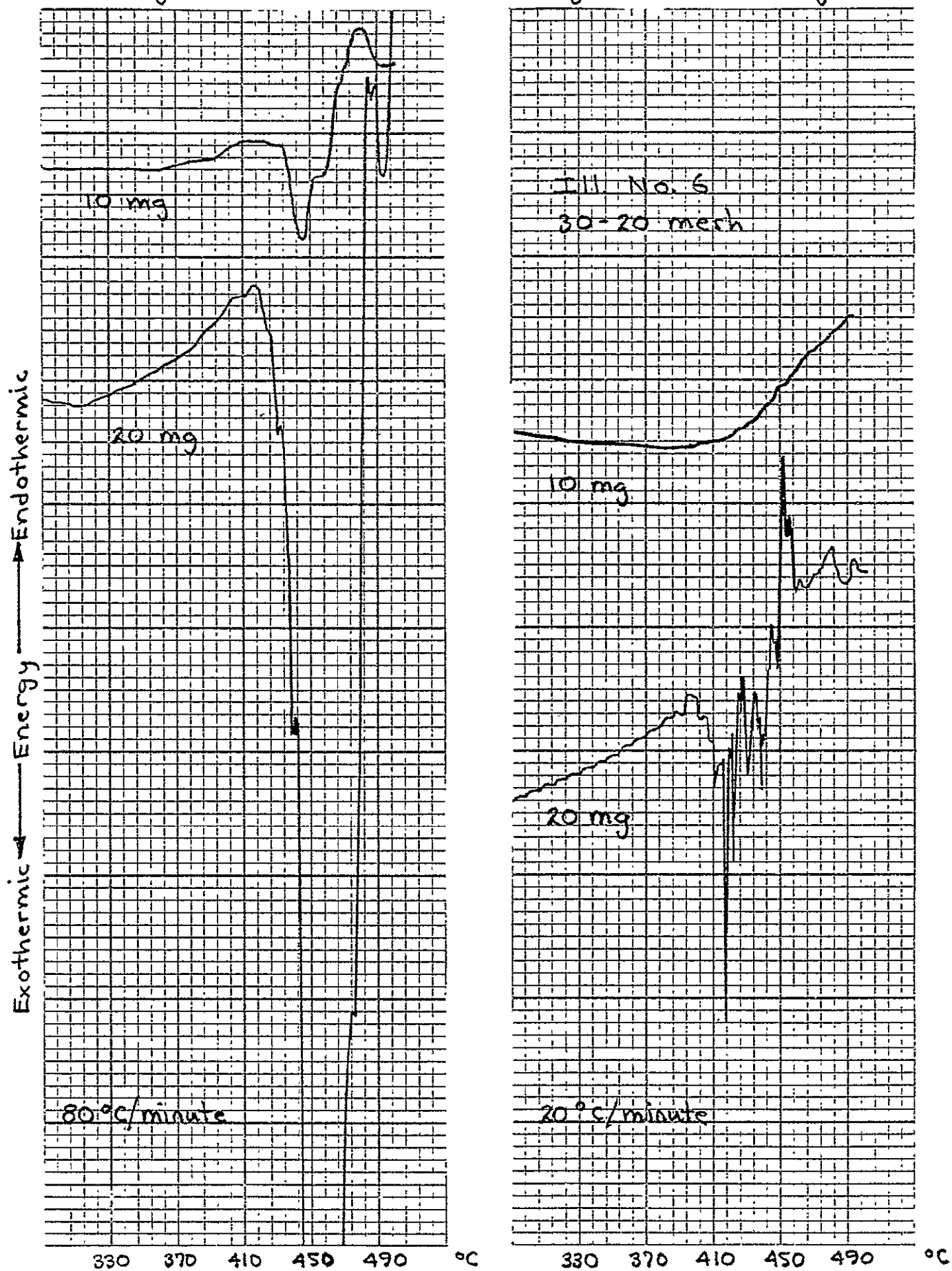
That is, the exotherm which was observed to decrease in magnitude with decreasing sample size, eventually disappeared at some small sample size at all heating rates. The discontinuous nature of this process could be verified by repeating the experiment using higher instrument sensitivities. In no case was an exotherm observed once the sample mass fell below this threshold.

It is difficult to interpret this observation, especially in the absence of a concurrent thermogravimetric analysis. In general, however, it seems probable that this behavior is another manifestation of the relationship of the exothermic peak to the production of volatile matter. It seems probable that the existence of an exothermic peak is associated with the manner in which volatile matter is evolved and allowed to accumulate within or is flushed out of the sample pan.

The effect of heating rate on the magnitude of the exothermic peak described above can best be rationalized on the basis of an analysis of the production of volatile matter as a function of temperature. At lower heating rates, volatiles are released at lower temperatures. The total amount of volatile matter produced is relatively independent of heating rate, although the maximum rate of loss occurs at lower temperatures for the lower heating rates. Furthermore, since the flow rate of inert diluent was held constant throughout, the rate of flushing of volatile matter out of the sample pan was relatively independent of heating rate. These circumstances would lead to a greater concentration of volatiles in the sample pan (at any temperature) at the higher heating rates. If this build-up of volatile material is essential to the occurrence of the exotherm, the absence of the peak at lower heating rates can be ascribed to the failure to achieve a sufficient concentration at higher temperatures due to flushing by the diluent gas. Moreover, the shift of the peak temperature upwards at higher heating rates can similarly be related to the shift of the maximum volatilization rate in the same direction.

Returning to the absence of an exothermic peak for smaller sample sizes, this too can be laid to the production of an insufficient concentration of volatile matter to sustain the exothermic reaction.

Figure 9-9: Effect of Sample Size on DSC Thermogram



The only evidence which seems to contradict this interpretation is the failure to detect volatiles until after the inception of the exothermic peak at the higher heating rates. As explained earlier, this was probably due to deficiencies in the instrumental methods employed. A more thorough thermogravimetric analysis is planned for next year's effort to confirm this interpretation.

9.4 Weathering Effects

The background of research into the effect of weathering on the thermal properties of coal was presented in Section 7. In this project, attention was focused on the influence of oxidation or weathering of coal samples on the exothermic peak observed in the plastic region. To this end, a number of specific tests were performed:

In an earlier paragraph, it was observed that coal samples containing mostly fines exhibited much diminished exothermic peaks, which disappeared entirely for samples passing through 100 mesh. This was laid to the increased effects of weathering on small particle-size samples. Many of the coal samples tested had been stored for as long as three years after having been ground to -10 mesh subsequent to sampling. A sample of lump coal (Illinois No. 6, HVC) was ground to pass -10 mesh, and a series of thermograms were obtained for comparison with thermograms of the same coal ground and stored some months previously.

The results of this test are depicted in Figure 9-10 wherein thermograms of the fresh and aged coals are compared. The exothermic peaks of the freshly ground coal are clearly evident for all of the particle size distributions shown. The aged samples, on the other hand, display substantially diminished exothermic peaks. A similar diminution of the endothermic devolatilization peaks is observed. It is clear that any quantitative interpretation of the energy absorption or evolution accompanying these processes must account for weathering effects.

Many of the coal samples tested had a substantial moisture content. Since the removal of this moisture was responsible for a substantial endothermic peak during the DSC scan, it was deemed advisable to remove the water by preheating at low temperatures prior to the start of a scan. The results of this procedure are depicted in Figure 9-11. Figure (A) represents a typical scan including a very substantial endothermic water removal peak. Figure (B) represents the resultant thermogram when a similar coal sample was preheated at 100°C for 15 minutes prior to the start of the scan. The almost complete absence of the water removal peak is evident.

The possibility that such preheating could affect the exothermic

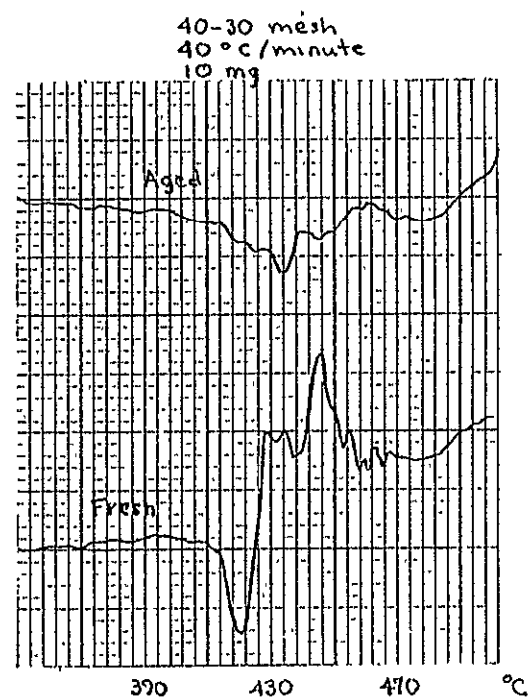
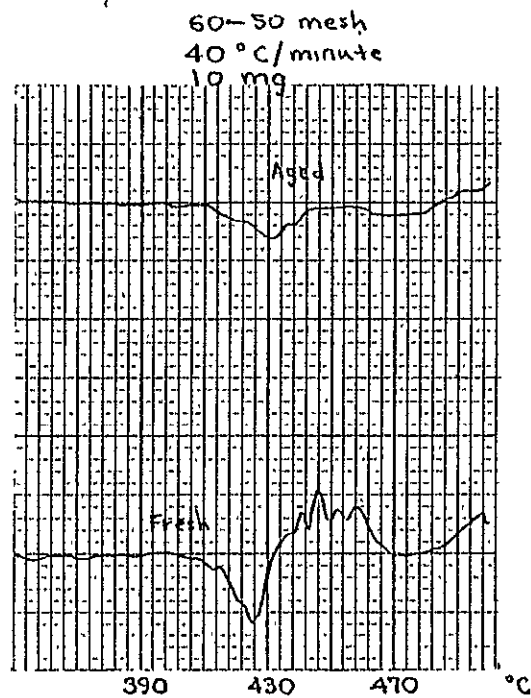
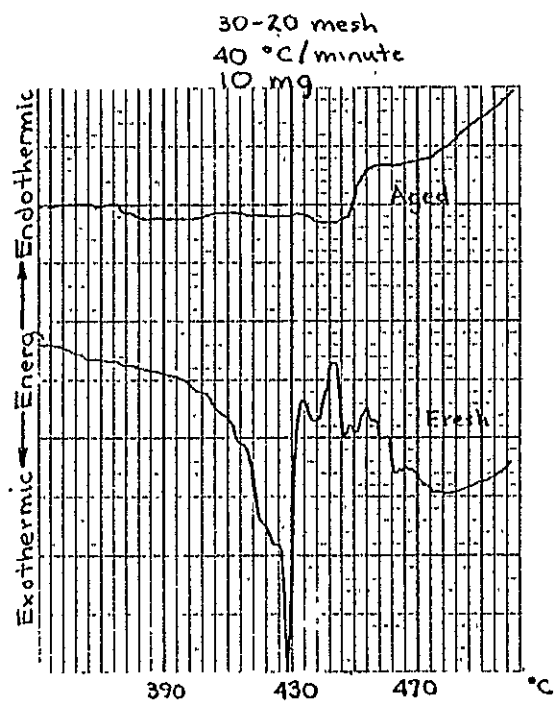
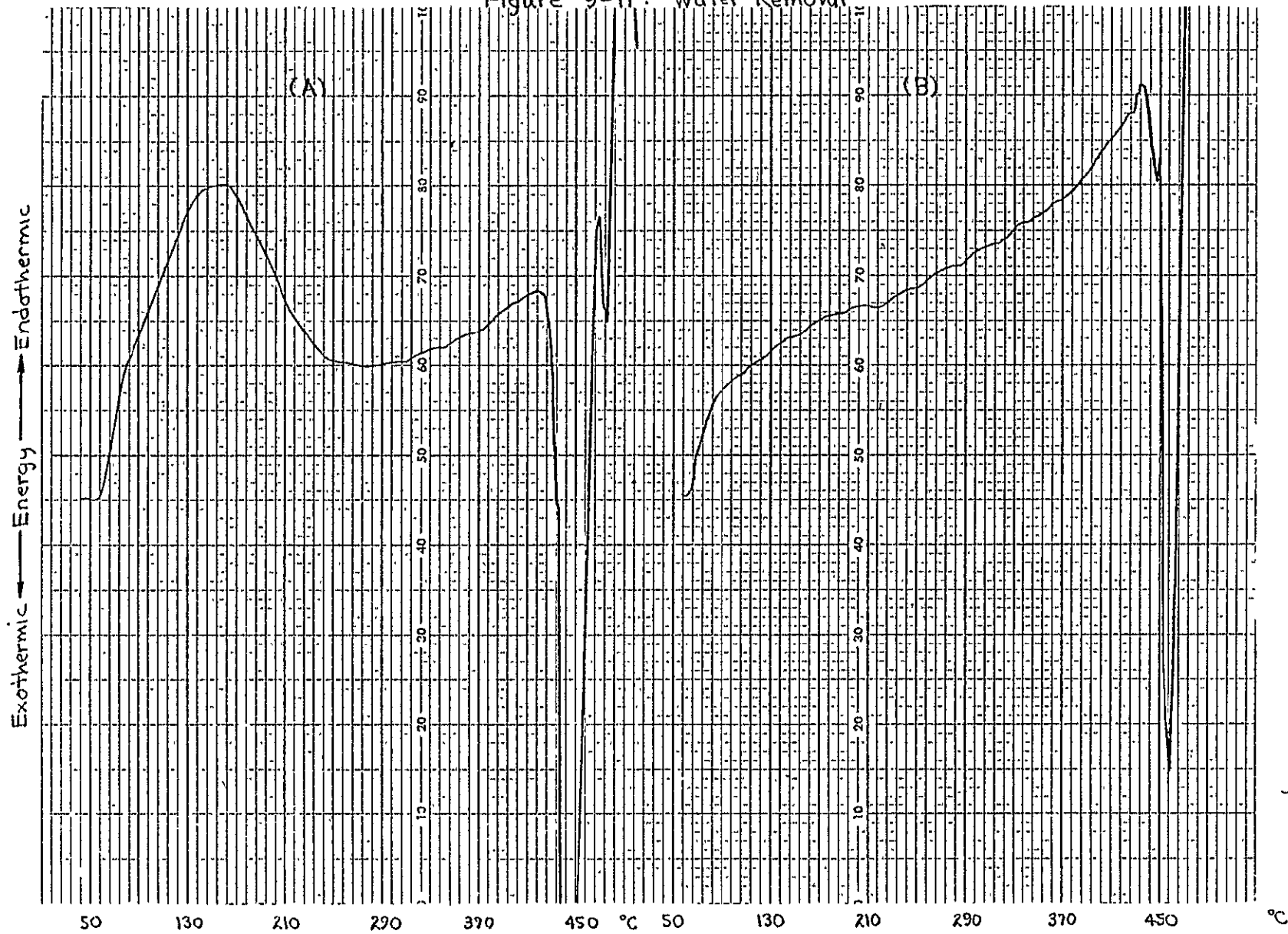


Figure 9-10: Aging Effects.

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Figure 9-11: Water Removal



peak was minimized by selecting a relatively low temperature for the water removal process. Preheating at higher temperatures could substantially reduce the amplitude of the exotherm as demonstrated in Figure 9-12. Coal samples were preheated for 30 minutes at various temperatures prior to commencing the DSC scan. Preheating at the lower temperatures had little effect on the exothermic peak. Preheating at temperatures at which devolatilization occurred lead to a decrease in peak amplitude resulting in the eventual disappearance of the peak for the low temperature char which had been heated to 450°C.

9.5 Calorimetric Analysis

Enthalpy changes associated with the exothermic and endothermic transitions during pyrolysis are calculated from the following relation

$$\Delta H = K \frac{ARb}{m}$$

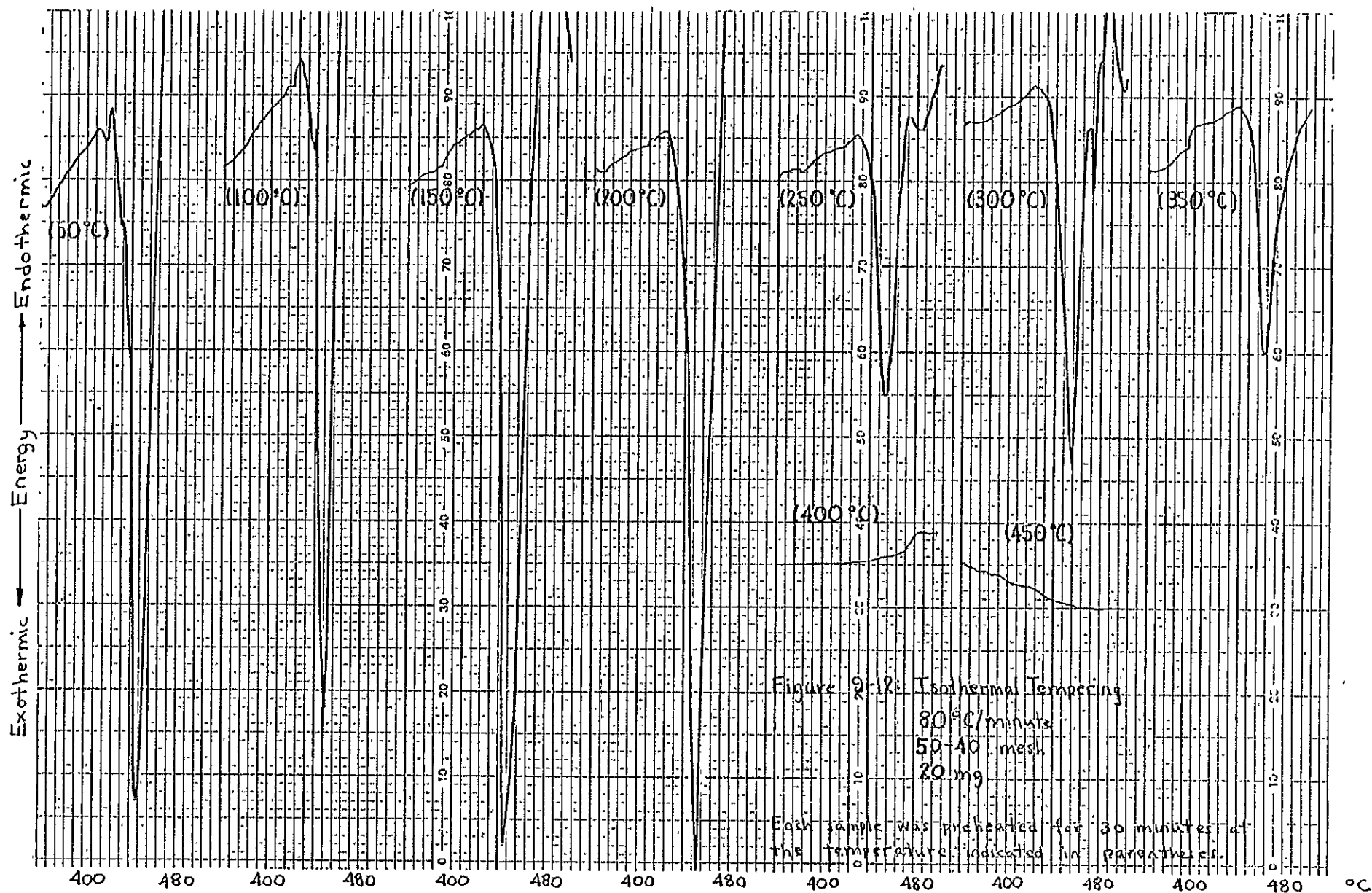
where ΔH is the enthalpy of reaction, A is the sample peak area, R is the instrument range setting, or y-axis sensitivity, and b is the linear time-base setting of the recorder. K is the instrument calibration constant. K can be obtained by measuring the peak area of a fusion transition of a known weight of a pure material of known heat of fusion using a convenient range setting and recorder chart speed.

Calibration of the instrument using the materials listed in Table 9-2 revealed no systematic effect of temperature on the computed value of K. This confirms the results of Brennan and Gray (24) who calibrated a Perkin-Elmer DSC-2 using a specific heat standard (sapphire). Moreover, Brennan and Gray detected no sample weight or heating rate dependence for the calibration constant.

Table 9-2
DSC Calibration Standards

Material	Fusion Temperature (°C)	ΔH_{fus} (mcal/mg)
Indium	156.6	6.80
Tin	231.9	14.45
Lead	327.5	5.50
Zinc	419.5	25.9

Contamination of the sample holder as a result of repeated coal pyrolysis runs did prove to be a factor in this research. To counter these effects, the practice of periodically cleaning and recalibrating the system was adopted.



During the pyrolysis of coal, there is a gradual weight loss over the entire temperature range. The displacement of the DSC output curve relative to the instrument reference base line is proportional to sample mass. As the mass of coal decreases with increasing temperature, the displacement of the output curve relative to the base line will vary continuously. Thus, the output curves cannot be integrated to yield reaction enthalpies per unit sample weight using the above equation unless the output curve can be corrected for weight changes during pyrolysis (23).

During the first year of effort reported herein, no continuous thermogravimetric analysis capability was available. An estimate of these effects was made by measuring the total weight loss of a number of samples over the entire pyrolysis run from 50-500°C. Table 9-3 shows the results of a total of 132 such tests. The percent weight loss shown correlates roughly with sample volatile matter content. Because of the large average weight loss (as much as 40% for PSOC 414) a quantitative analysis of these results was not attempted.

Also shown in Table 9-3 are the results of 30 tests in which the weight loss of the reheated low-temperature char was determined. In no case did the char weight loss exceed 2%.

Table 9-3
Thermogravimetric Analysis

Coal Sample	No. In Test	Initial Pyrolysis	No. In Test	Reheated Char
		Avg. Wt. Loss (%)		Avg. Wt. Loss (%)
233	3	26.88	1	0.96
238	13	28.87	6	1.02
300	2	22.51		
310	5	29.84	1	1.3
314	5	26.52	5	0.94
316	5	26.15	1	0.03
318	2	8.75		
414	10	40.40	6	1.70
Ky. No.9	15	26.11	5	1.37
Ill.No.6	72	27.58	5	0.93

10. Recommendations

Differential Scanning Calorimetry (DSC) studies performed during the first year of this project demonstrated the occurrence of exothermic transitions in selected coal samples. These transitions were observed within or immediately below the plastic range associated with a production of volatile matter.

The quantitative calorimetric analysis of these transitions was not possible because of the absence of corresponding weight loss data as explained previously. Furthermore, no conclusive explanation of the physical and/or chemical mechanism responsible for these transitions could be drawn. As a result, a number of specific objectives and recommendations for future emphasis are presented here.

10.1 Thermal Analysis of Coal

Differential Scanning Calorimetry (DSC) is a technique in which the ordinate of the output curve at any temperature is directly proportional to the differential heat flow between the sample and a reference material and in which the area under the measured curve is directly proportional to the total differential heat input. The term 'scanning' implies that the temperature of both the sample and reference is increased at a programmed rate. If the instrument is calibrated with a reference material having a known specific heat as a function of temperature, or with a series of materials with known melting points and latent heats, the area under the measured curve becomes proportional to the rate of energy absorption (or evolution) of a fixed mass sample. The displacement of the DSC output curve (relative to the base line) is proportional to sample mass.

During the pyrolysis of coals, there is a gradual and continuous weight loss over the entire temperature range. As the mass of coal decreases with increase of temperature, the displacement of the output curve relative to the reference base line will vary continuously. Therefore, although the output curves can be integrated to yield enthalpy change values, these cannot be expressed per unit weight, or converted to specific heat data, unless the output curve can be corrected for weight changes occurring at different temperatures.

Thermogravimetric Analysis (TGA) is another technique for studying physical and chemical changes in a material. In contrast to the measurement of energy changes in DSC, TGA provides a continuous measurement of sample weight as a function of sample temperature as that temperature is raised at a uniform rate. The resulting output curve of weight against temperature is called a thermogravimetric curve. Weight changes during pyrolysis, under conditions simulating those in the DSC runs can be obtained, therefore. The combination of DSC and TGA provides a quantitative tool for measurement of thermal effects involved in the pyrolysis of coals.

Devolatilization is a continuous process during pyrolysis. It is the primary devolatilization stage (350-550°C) in which compounds containing carbon, hydrogen, and oxygen are released, which is associated with the plastic range of coal. When the coal is heated at a constant heating rate, the devolatilization rate in the primary devolatilization stage passes through a maximum. This maximum shifts toward higher temperatures with an increase in heating rate. It is suggestive that a similar shift with heating rate occurs in the measured plastic properties of coal and in the characteristic exothermic transition observed in some coal samples during the first year of this project. Figure 10-1 depicts a typical relationship between the maximum devolatilization rate and the maximum plasticity of the same sample of coal. The effect of heating rate on devolatilization rate and on plasticity are shown in Figures 10-2 and 10-3. Figures 10-1 to 10-3 have been adapted from Reference (9). The effect of heating rate on the thermal transitions observed in a typical coal sample in this laboratory is shown schematically in Figure 10-4.

The association of gas evolution with specific peaks on a DSC curve helps to distinguish between physical and chemical transitions. Hence, gas detection is often coupled with DSC and/or TGA, the gas evolution curve and the DSC or TGA curve being measured simultaneously on one sample. Evolved Gas Analysis (EGA) is a technique in which the evolved volatiles are separated, the individual components identified and their relative amounts measured. A sampling device is included in the DSC and/or TGA effluent to the analyzer. The analysis itself may be performed intermittently or continuously. The commonest analyzers are gas-liquid chromatographs, infrared spectrophotometers, and mass spectrometers.

The major thrust of this research should be aimed at developing a combined DSC/TGA/EGA system for the purpose of quantitative thermal analysis of selected coal samples. Particular attention should be focused upon the quantitative determination of specific heats and heat effects associated with physical and chemical changes taking place within the plastic region of coal. In addition, this system could be used to study possible oxidation or weathering of coal during storage and as a result of standard ASTM drying procedures as described below.

10.2 Objectives of Proposed Research

The objectives of the proposed research are:

- (1) Application of experimental thermal analysis techniques of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Evolved Gas Analysis (EGA) by Gas-Liquid Chromatography (GLC) to study the thermal properties of coal within and below the plastic region of coal.
- (2) Application of DSC, TGA, and EGA techniques to the evaluation of possible degradation effects of ASTM coal drying procedures.

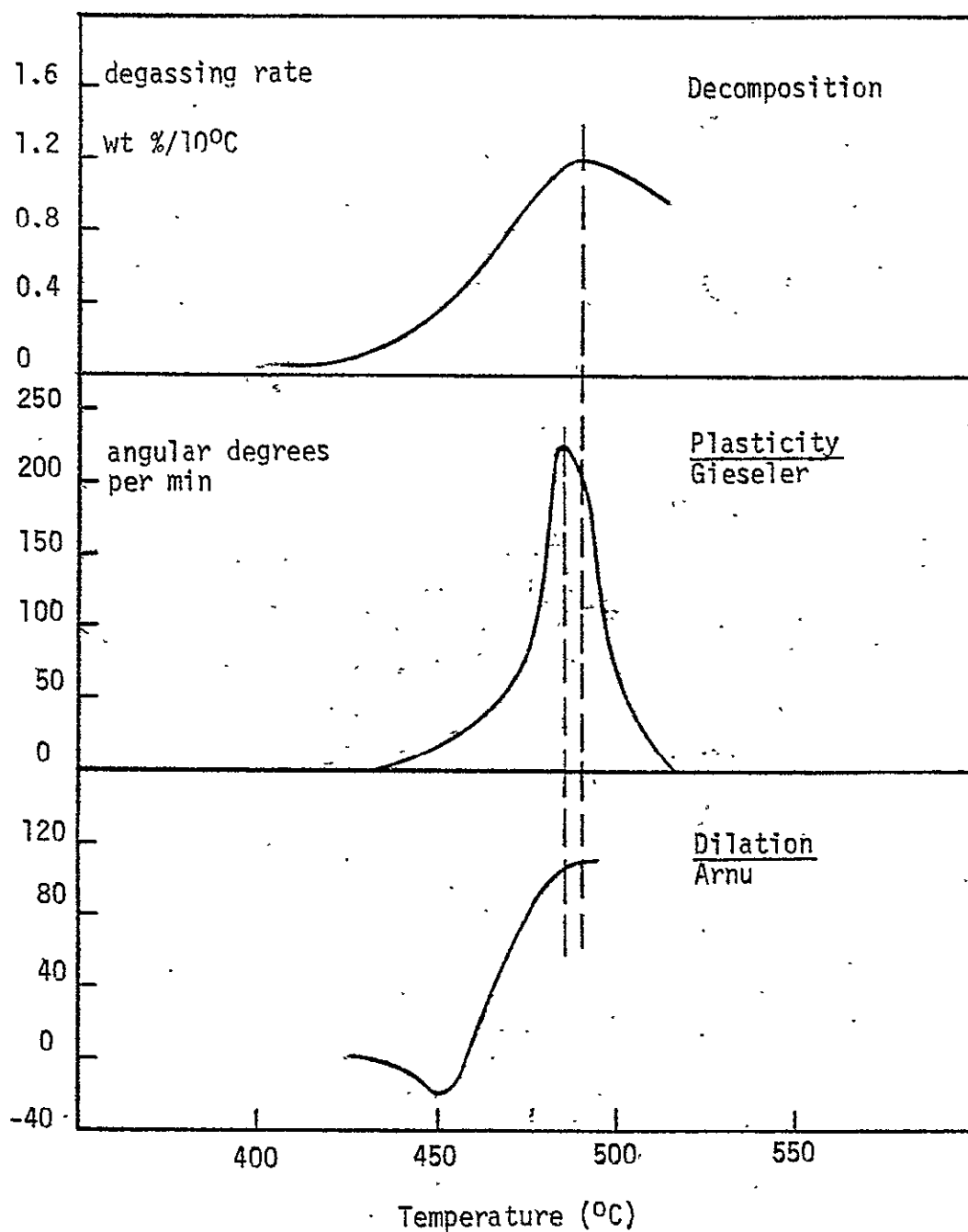


Figure 10-1

Characteristic Temperatures in the Decomposition, Plasticity and Dilation Curves (Heating Rate 30°/min) Reference (9).

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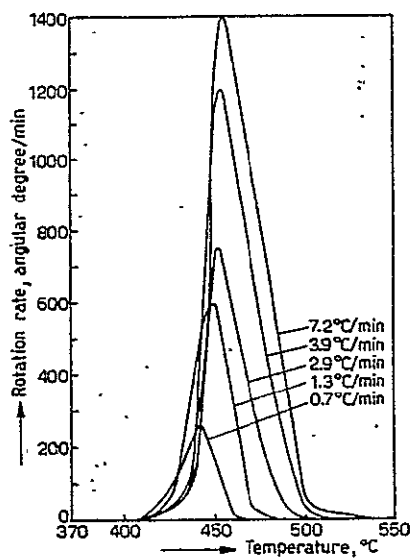


Figure 10-2

Giesler Curves at Constant Heating Rates. Medium-Volatile Bituminous Coal, 24% VM. Reference (9).

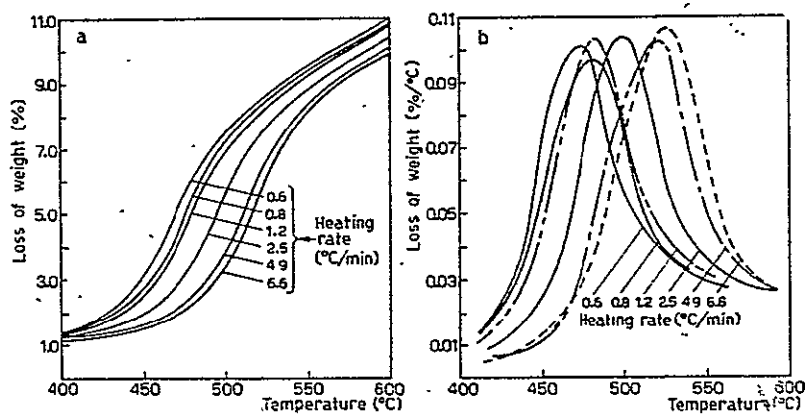
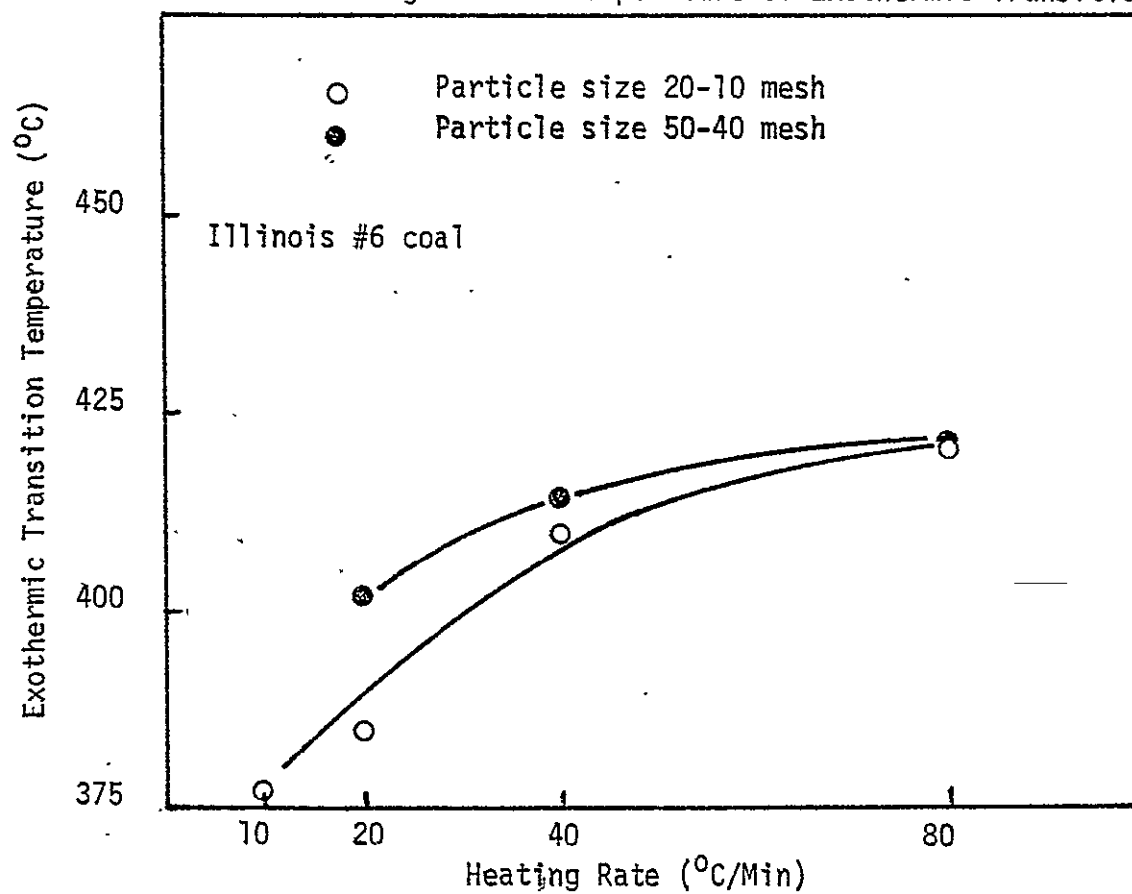


Figure 10-3

Decomposition at Different Heating Rates. Low-Volatile Bituminous Coal, 18% VM. Reference (9).

Figure 10-4
Effect of Heating Rate on Temperature of Exothermic Transition



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- (3) Application of DSC, TGA, and EGA techniques to the evaluation of possible degradation or "weathering" of coal stored under various controlled conditions.
- (4) Application of DSC, TGA, and EGA techniques to a direct kinetic examination of coal oxidation.

10.3 Work Plan

The work necessary to meet these objectives can be conveniently divided into district tasks as described in the following paragraphs.

Task 1. Thermal Analysis of Selected Coals.

Statement: Experimental thermal analysis of coal using Differential Scanning Calorimetry (DSC) Thermogravimetric Analysis (TGA), and Evolved Gas Analysis (EGA) techniques.

Outline: Continue detailed experiments initiated during the first year of this project to determine the enthalpy and kinetics of observed physical and chemical changes over the temperature range of ambient to approximately 500°C. Emphasis would be placed on the plastic region of coal (390°-490°C). Examine the effects of such parameters as heating rates, sample particle size, pressure, isothermal tempering. Thermogravimetric Analysis and Evolved Gas Analysis by Gas-Liquid Chromatography would be included. Although the primary objective of this task would be the determination of enthalpy changes associated with the pyrolysis process, the combination of DSC, TGA, and EGA techniques would provide an opportunity to investigate the mechanism responsible for the observed thermal effects. Specifically, this would include the determination of volatilization rates as a function of temperature and heating rate. The volatilization temperature range and its relation to the appearance of endothermic and exothermic transitions would be studied. Through the use of EGA, an analysis of pyrolysis products could be made.

Task 2. ASTM Procedures.

Statement: Experimental determination of possible degradation effects of ASTM coal-drying procedures and proximate analysis of coal using DSC/TGA/EGA techniques.

Outline: ASTM Standard Method of PREPARING COAL SAMPLES FOR ANALYSIS (D2014-68) specifies air drying as a process of partial drying of coal to bring near to equilibrium with the ambient atmosphere. It is possible that this process can lead to a degradation of the sample, particularly with easily oxidized coals. It is proposed to investigate this question by considering the following parameters:

- a. Particle size or distribution
- b. Drying time
- c. Drying temperature
- d. Drying atmosphere (air, inert gas)
- e. Coal type

The evaluation of this effect would be made on the basis of DSC techniques in conjunction with TGA and EGA investigations as described in Task 1. DSC measurements would be sensitive to small changes in thermal characteristics (i.e. possible endothermic or exothermic reactions) resulting from oxidation of the sample. TGA and EGA measurements also would provide an indication of the extent of oxidation occurring during the drying procedure.

ASTM STANDARD METHODS OF LABORATORY SAMPLING AND ANALYSIS OF COAL AND COKE (D271-68) establishes methods to determine the proximate analysis of a coal sample to include percents water, volatile matter, fixed carbon, and ash. Fyans (25) has demonstrated the application of TGA as an alternative to the ASTM proximate analysis. It is proposed to obtain a proximate analysis of all samples tested employing TGA.

Task 3. Degradation of Coal Stored Under Various Conditions.

Statement: Experimental determination of "weathering" or degradation of stored coal using DSC/TGA/EGA techniques.

Outline: Storage of coal may also lead to degradation of the sample depending upon the conditions of storage. DSC/TGA/EGA measurements can be useful in detecting such effects. It is proposed to investigate these effects by considering the following storage conditions or parameters:

- a. Particle size or distribution
- b. Storage time
- c. Storage temperature
- d. Storage atmosphere (air, inert gas) and humidity
- e. Coal type

Task 4. Oxidation Studies.

Statement: Application of DSC/TGA/EGA analysis to a direct kinetic examination of coal oxidation.

Outline: The combination DSC/TGA/EGA analysis should prove to be a sensitive measure of oxidation in coal. The DSC/TGA/EGA system could be used to study the oxidation kinetics of coal with a view of correlating the observed behavior with coal plasticity. Particular attention should be focused on the effect of very low oxygen concentration on pyrolysis reactions.

11.0 References

- (1) England, C., and P. R. Ryason, "A New Method for Continuous Injection of Coal," Jet Propulsion Laboratory, May 1, 1975.
- (2) England, C., and P. R. Ryason, "Coal Extrusion in the Plastic State," a paper presented at the Conference on Coal Feeding systems, California Institute of Technology, Pasadena, California, June, 1977.
- (3) Hobday, J. M., "Development of Coal-Feeding Systems at the Morgantown Energy Research Center," Conference on Coal Feeding Systems, California Institute of Technology, Pasadena, California, June, 1977.
- (4) "Coal Pump Development and Technical Support Quarterly Project Report No. 4," Report No. 5030-144, Jet Propulsion Laboratory, Pasadena, California, November, 1977.
- (5) Loison, R., et. al., "The Plastic Properties of Coal," in Chemistry of Coal Utilization, Supplementary Volume, H. H. Lowry, ed., Wiley, New York, 1963.
- (6) Hollings, H., and J. W. Cobb, "A Thermal Study of the Carbonization Process," Fuel, 2, 322 (1923).
- (7) Glass, H. D., "Investigation of Rank in Coal by Differential Thermal Analysis," Econ. Geol., 49, 294 (1954).
- (8) Glass, H. D., "Differential Thermal Analysis of Coking Coals," Fuel, 34, 253 (1955).
- (9) Van Krevelen, D. W., "Coal," Elsevier, Amsterdam, 1961.
- (10) Whitehead, W. L., and I. A. Breger, "Vacuum Differential Thermal Analysis," Science, 111, 279 (1950).
- (11) Breger, I. A., and W. L. Whitehead, "Thermographic Study of the Role of Lignin in Coal Genesis," Fuel, 30, 247 (1951).
- (12) King, L. H., and W. L. Whitehead, "Vacuum Differential Thermal Analysis of Coal," Econ. Geol., 50, 22 (1955).
- (13) King, L. H. and D. G. Kelley, "Investigation of the Coking Properties of Coal by Vacuum Differential Thermal Analysis," Econ. Geol., 50, 832 (1955).

- (14) Berkowitz, N., "On the Differential Thermal Analysis of Coal," *Fuel*, 36, 355 (1955).
- (15) Clegg, K. E., "Some Experimental Factors That Modify Differential Thermograms of Bituminous Coal," Illinois State Geol. Survey Rept. of Inv. 190, 30 pp. (1955).
- (16) Gaines, A. F., and R. G. Partington, "Differential Thermal Analysis of Mixtures of a Low Rank Coal and Various Inorganic Compounds," *Fuel* 39, 193 (1960).
- (17) Pampuch, R., and B. Roga, *Prace Glownego Inst. Gorn. Ser. B. Komm.*, 183 (1956).
- (18) Kroger, C., and A. Pohl, *Brennstoff-Chem.* 38, 179 (1959).
- (19) Boyer, A. F., and P. Payen, 3rd Intern. Conf. on Coal Science, Valkenburg, 1959.
- (20) Kessler, M. F., and H. Ramovackova, "Experience with Differential Thermal Analysis of Coal and Coke," *Fuel*, 40, 161 (1961).
- (21) Stephens, J. N., "Continuous Measurement of the Enthalpy of Coals," *Fuel*, 42, 179 (1963).
- (22) Smith, J. W., and D. R. Johnson, "Thermal Analysis of Natural Fuels," Proceedings of the Second Toronto Symposium on Thermal Analysis, Toronto, 1967.
- (23) Mahajan, O. P., A. Tomita, and P. L. Walker, Jr., "Differential Scanning Calorimetry Studies on Coal. 1. Pyrolysis in an Inert Atmosphere," *Fuel*, 55, 63 (1976).
- (24) Brennan, W. P. and A. P. Gray, "The Calorimetric Precision and Accuracy of A Scanning Calorimeter," Thermal Analysis Application Study No. 9, Perkin-Elmer Corporation, Norwalk, Conn., 1973.
- (25) Fyans, Richard L., "Rapid Characterization of Coal by Thermogravimetric and Scanning Calorimeter Analysis," Thermal Analysis Application Study No. 21, Perkin-Elmer Corporation, Norwalk, Conn., 1977.

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