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Thermogravimetric Analysis of Coal Blends Under Conditions of Pyrolysis & Combustion

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Yaodong

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THERMOGRAVIMETRIC ANALYSIS OF COAL BLENDS UNDER CONDITIONS OF PYROLYSIS AND COMBUSTION

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Yaodong Gan
August 1989

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THERMOGRAVIMETRIC ANALYSIS OF COAL BLENDS UNDER CONDITIONS OF PYROLYSIS AND COMBUSTION

Recommended August 14 1989
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Yaodong Gan August 1989 109 pages

Directed by: W.P. Pan, J.W. Reasoner, and J.T. Riley

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In recent years, the growing attention to coal quality by coal-burning utilities has led to an increase in coal blending. Coal blending is done with both economics and the quality of coal in mind. To assess the quality of coal, pyrolysis and combustion influencing thermal parameters, as measured in thermogravimetric analysis (TGA) experiments can be applied. The coal industry needs a study to determine relationships that may exist between the measured values of TGA thermal parameters in individual coals and those in the blends. The TGA thermal parameters are the weight loss, T_{max}, T_i, $T_{1/2}$, t_{max}, $t_{break\ point}$, $t_{combustion\ end\ point}$, R_{max} and residue. With these relationships, there exists the possibility of accurate prediction of values of these parameters in the coal blends. In this study, a series of coal blends were prepared and thermal parameters for the blends were measured to examine the additive or nonadditive nature of results obtained under both pyrolysis and combustion conditions using thermogravimetric analysis.

INTRODUCTION

Coal is widely employed as an energy source. In the U.S, the major use of coal is for electric power generation. Fuel oil is used to generate approximately 15% of the nation's electricity (1). It is possible, however, with present technology along with new developments in coal combustion to reduce reliance on petroleum-based fuels by replacing them with coal. In recent years, one of the major potential problems in the world is a shortage in the petroleum supply. With this shortage, coal becomes a more important energy source for industry as well as for daily human existence. The U.S. contains vast quantities of low rank coal, the use of which has been increasing nationally. Present estimates put these deposits at approximately 38 billion tons (1), and indicate that a major portion of the total coal production in the U.S. by 1990 will be low rank coals. In order to improve the application of low rank coal and to make it a major potential energy source in the next century, different technologies have been developed (1,2). These technologies are affected by the behavior and quality of low rank coal. In particular, greater attention to coal quality by coal-burning utilities (3-5) has resulted in an increase in coal blending in recent years.

A. Coal Blends

Coal blends are made from two or more types of coal using different proportions of each. The cost and availability of the desired coals are a principal economic consideration. Generally, the quality of coal or blended coal is assessed by certain pyrolysis and combustion influencing parameters (6).

The current practice for determining the overall quality of blended coals is to use the weighted average of the determined values for the individual coals in the blend (7-10). This practice may give accurate composite values for the moisture, sulfur, and heating value content of the coal blend, but not for the volatile matter and ash. The calculated composite values for other coal blend parameters, such as the grindability, ash fusibility, and free-swelling index, are not reliable (3,11-13).

Consequently, the results obtained in these tests are often not additive and calculated weighted averages for coal blends should only be used with some reservations about their accuracy (14). It may be possible, however, to establish relationships between certain elemental values for the individual coals and a measured parameter for the blended coal. For instance, the ash fusion temperatures of certain coal blends have been predicted, within allowable tolerances, using the composition of the ash from the individual coals used in the blends (15-17).

In the field of coal blend analysis, a pioneering study has been carried out by Riley and his co-workers (14) to investigate parameters of coal blends, such as moisture, ash, volatile matter, carbon, hydrogen, nitrogen, total sulfur, etc. Their studies have shown that some of the parameters of coal blends, such as the ASTM volatile matter, free-swelling index (FSI), and Hardgrove grindability index (HGI), do not exhibit additive relationships. Some general conclusions can be drawn on the observed differences between the measured and calculated analytical values for coal blends used in this study:

(1) The dry ash and ASTM D 3175 dry volatile matter values determined for coal blends are generally higher by averages of 0.36% and 1.04% than the calculated ash values.

(2) The LECO MAC-400 dry volatile matter values determined for coal blends are generally lower by an average of 0.26% than the calculated values.

(3) The Hardgrove grindability indexes for blends of coals with HGI values varying by less than 10 units are additive. Blends of coals with HGI values varying by more than 10 units appear not to be additive.

(4) The free-swelling index values for coal blends are apparently not additive.

(5) The analytical values for coal blends that appear to be additive are the moisture, carbon, hydrogen, nitrogen, and sulfur values.

For our study, we wanted to establish whether or not the nonadditive relationship also applies for other thermal parameters of coal blends. Our research was designed to determine the variation of certain coal blend parameters using thermogravimetric analysis. The thermal parameters obtained in the laboratory experiments can be used to predict the relative performance of coals on a large scale in power plants. Therefore, the study of thermal parameters of coal or blended coal is important for the efficient operation of power plants.

B. Thermogravimetric Analysis (TGA)

Physical properties of coal are measured to obtain information on the structure of coal. A number of different spectroscopic methods such as UV, IR, NMR, ESR, x-ray fluorescence, atomic absorption, MS, and x-ray diffraction, as well as thermal analysis, can be applied for this purpose (18). Thermal analysis methods, by which the occurrence of physical and chemical transformations can be measured as a function of temperature (or time), have been widely used to understand the characteristics of coal pyrolysis and combustion (19). Thermogravimetric analysis (TGA) measures the mass change as a function of temperature (or time) in a given atmosphere. A TG curve can be seen in Figure 1. It plots percent weight loss (Y axis) versus temperature (X axis). The first derivative with respect to time of mass variation (dm/dt) can also be obtained from the TGA results. This is indicated by the dotted line in the figure. This is called the differential thermogravimetric curve and is used because of its greater sensitivity. Differential thermogravimetric (DTG)

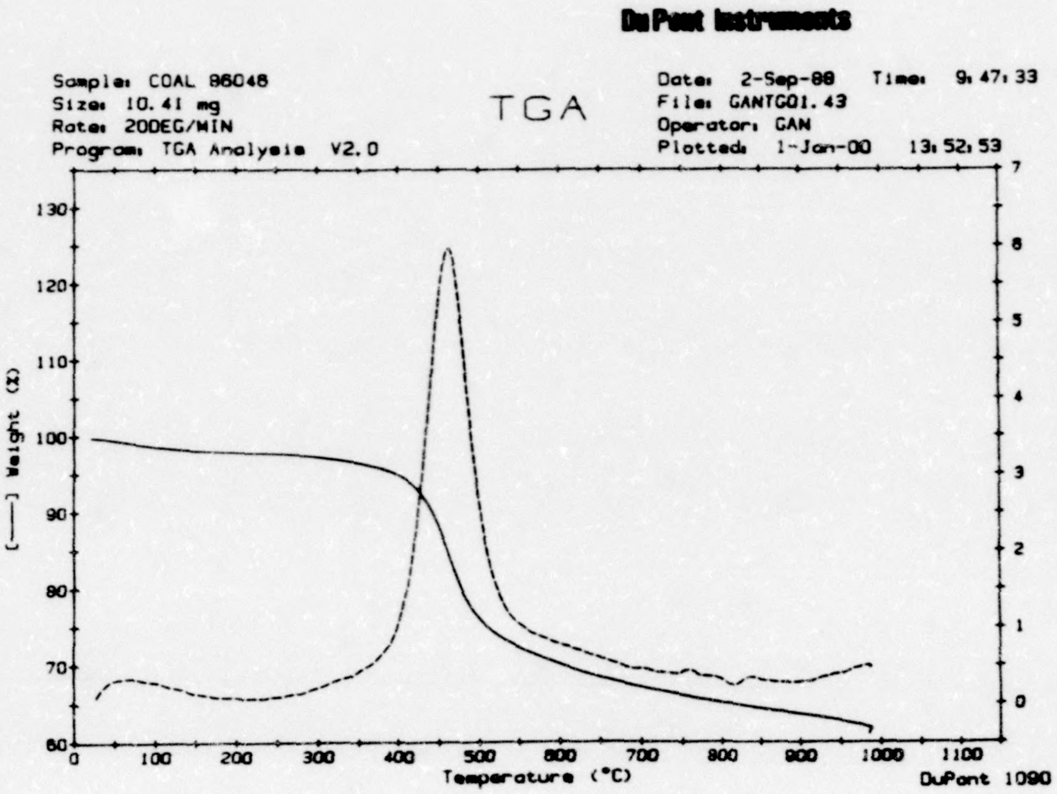

Figure 1. TG Heating Curve - HV1 Coal in Nitrogen under Non-isothermal Conditions.

plots the rate of weight loss against the temperature. Several advantages of using the DTG curve rather than the TG curve are summarized as follows (20): (1) the DTG curve is more accurate in showing a small mass loss during the reaction; (2) overlapping reactions are better defined by DTG; and (3) the temperature (T_{max}) which indicates the maximum mass loss, can be defined more exactly for each reaction zone.

Depending on what kind of information is needed, three different operating modes for TGA may be used (20). First is isothermal thermogravimetry, in which any change in mass as a function of time is measured by the TGA curve at constant temperature. Second is quasi-isothermal thermogravimetry where the sample is heated to constant mass at each of a series of increasing temperatures. Third is non-isothermal or dynamic thermogravimetry, where the sample mass is recorded as a function of temperature, which changes at a linear rate in a controlled atmosphere. The TG curve (i.e. mass loss curve, Figure 1) gives information concerning the thermal stability of a sample, and an indication of the intermediate compounds that may be formed during thermal decomposition of the sample.

A wide range of applications for thermogravimetry have been outlined in numerous reviews and books (20). Even with its limitations and sources of error, the technique of thermogravimetry is a useful one. The TG technique gave reproducible results when the proximate analysis of coal was studied (20). Thermogravimetry has been found to be useful as a rapid and convenient tool for screening coals using the proximate analysis of coal samples. In nitrogen, volatile matter and moisture are lost at temperatures up to 1000 °C; and on changing the atmosphere to oxygen, fixed carbon is burned off leaving the ash as residue (20). Thus, from a single sample, usually 10-30 mg, the moisture, volatile matter, fixed carbon, and ash can be determined (20). A detailed investigation of the thermal characteristics of six Kentucky bituminous coals were studied by TG analysis (21). These data agree within limits of experimental error to those determined by the ASTM method.

Yoshida, and co-workers (22) established a routine method for the analysis of coal by TGA. Analytical results of 11 samples of domestic and foreign origins were in close agreement with those determined by the Japanese standard analytical method.

A comparison of proximate analysis results obtained by Cumming and McLaughlin using the thermobalance with those established using the British Standard method were similar (23). Fourteen coal samples of widely differing properties were used in the study.

All previous studies indicate the TGA technique produced results comparable to those obtained with classic standard methods. Thus, TGA is a suitable method for coal analysis.

C. Coal Pyrolysis and Combustion

In recent years, TGA has been used to study the pyrolysis and combustion processes of coal for further understanding of the properties of coal. Although the exact nature of the coal combustion process, including coal volatiles combustion kinetics, is still not well understood, it can be split into two main processes: (1) degradation of hydrogen containing components with the evolution of volatiles (pyrolysis) and their subsequent combustion; and (2) degradation of the predominantly carbon species with heterogeneous combustion of the solid char (24-26). Not only will moisture and CO_2 be removed in the first stage of pyrolysis, but also some cross-links will break and some of the functional end groups will be removed (24). Further heating releases the volatile matter of coal producing hydrogen-rich and oxygen-rich species such as hydrogen, methane, carbon monoxide, carbon dioxide and steam (27), leaving a low volatile matter char containing small carbon crystallites and graphite (24). The heating rate, coal rank, particle size, ambient atmosphere and inorganic constituents will effect the nature and proportions of the pyrolysis products (25,28). In the case of temperature, the following gases are released in the volatile material at a low heating rate: H_2O, CO_2, CO, CH_4, C_2H_6, H_2 and N_2. These are generally observed in the order given when the temperature is increased from 400°C - 800°C (29). The yield of volatile substances using rapid heating rates is higher than that from slow heating rates. This difference is due to the formation of the cross-linked material during pyrolysis using a low heating rate. This cross-linked material is unable to escape as volatile matter, causing a lower volatile yield (25).

Pyrolysis occurs to some extent in all coal conversion processes. Char combustion is much slower than the rate of release and combustion of the volatiles (24,30). However, it is believed that some overlapping will occur between the pyrolysis process and char combustion (30). Separating the pyrolysis stage from the char combustion step to overcome this difficulty has been suggested (30). First, the coal is pyrolyzed under controlled conditions, then the char combustion is investigated. Char combustion can be described as graphite combustion with complications (24). In the work reported in this thesis we studied the coal blends in atmospheres of nitrogen and air to gain a better understanding of the processes of coal pyrolysis and combustion.

Differential thermogravimetry (DTG) has been widely used for several years to study the behavior of coal during combustion and devolatization. The profiles obtained are considered to be characteristic of a given solid fuel. The burning profile (DTG) is a useful measure of the combustion characteristics of fuel. It provides information on oxidation rates from ignition to completion of burning.

Morgan and co-workers used TGA methods for coal combustion studies (31,32). Their work examined the dependence of the coal burning profile on test conditions and coal characteristics. A good correlation has been found between characteristic temperatures of the profiles and unburnt fuel loss during combustion. Thus, burning profiles provide a valuable and rapid method of ranking coals in terms of their burnout performance. The authors concluded that the TGA technique provides a rapid quantitative method of measuring the proportions of vitrinite-char and inertinite-char from low rank bituminous coals.

A TG study of kerogen combustion in the presence of calcium oxide was reported by Elder and Reddy (33). An investigation of the combustion of a western Kentucky bituminous coal in the presence of calcined limestone has been made using rapid heating non-isothermal TG. This rapid procedure is confirmed as a means for screening naturally occurring limestones for sulfur retention purposes, irrespective of the relative proportions of fossil fuel and absorbent present.

The presence of some metal salts in mineral matter will invariably influence the burning characteristics of the blended coal. Serageldin and Pan (34) have studied the effect of $CaCl_2$ on char reaction kinetics. Their work involving metal-based salts is the third part in a series of studies related to boiler applications. The information obtained through their work is useful in understanding the effect of similar materials on the oxidative behavior of coal char. Serageldin and Pan (35) more recently reported the effect of $CaCl_2$ and $Ca(C_2H_3O_2)_2$ on the reactivity of a lignite coal at a low heating rate.

D. Activation Energy Determination by TGA

Thermogravimetry (TG) has been used for determining the activation energy of coal decomposition in the kinetic study of coal (20). Kinetic parameters (activation energy, order of reaction and frequency factors) can be obtained from TG and DTG curves by using isothermal or non-isothermal TG methods. The advantages of non-isothermal methods over isothermal methods are as follows (20):

(1) considerably fewer experimental runs are required;

(2) kinetic results can cover the whole temperature range;

(3) results obtained from isothermal methods are often questionable when the reaction releases significant energy which raises the surrounding temperature.

The disadvantage, however, of using non-isothermal TG methods, compared to isothermal methods, is that the reaction mechanism may be difficult to determine. Therefore, the results for the activation energy, order of reaction, and frequency factors give uncertain meanings (20).

Serageldin and Pan (36-38) discussed the usefulness of several non-isothermal methods to calculate the apparent activation energy of coal for kinetic studies of the thermal decomposition in relation to the pyrolysis kinetics of coal. Because of the extremely complex nature of coal, especially its combustion kinetics (39), the real activation energy is difficult to determine. For the apparent activation energy, however, the Arrhenius equation for a first order reaction is recommended for thermogravimetric analysis of coal (36).

For a first order process the following relationship holds true:

$$-(dW/dt)=K \cdot W \quad \text{(Equation 1)}$$

$$\text{or} \quad K=-(dW/dt)W^{-1}$$

where dW/dt is the instantaneous rate of weight loss, W is the weight of unreacted coal, and K is the specific reaction rate.

The specific reaction rate is related to temperature by the Arrhenius equation:

$$K=A \cdot \exp(-E/RT) \quad \text{(Equation 2)}$$

$$\text{or} \quad \log K=\log A-E/2.303RT \quad \text{(Equation 3)}$$

where A is the frequency factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Thus, if values of K can be obtained at various temperature levels, using Equation 1, the activation energy can be derived using Equation 3. In the present case, all the necessary values can be obtained from a single thermogravimetric scan where TG (sample weight) and DTG (rate of weight loss) outputs are plotted against sample temperature. Smith and co-workers (39) have applied this type of analysis to a large number of coal samples and found the following to be true. Arrhenius plots (log K versus 1/T), see Figure 2, have more than one linear region, with each region having its own associated value of apparent activation energy ($E_1, E_2, E_3, \ldots\ldots E_n$). This observation has been confirmed in the present work, and it was thus decided to use the concept of activation energy as a basis for characterizing the reactivities of coal samples. As described, the individual

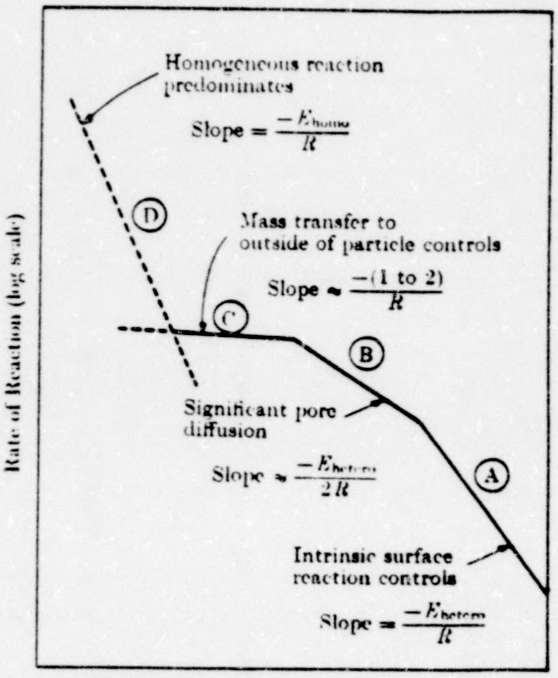

Figure 2. Possible Kinetic Regimes in a Gas-phase Reaction Occurring on a Porous Solid Catalyst.

values of E_1, E_2, etc. can be attributed to different reaction mechanisms coming into play as the temperature is increased. Furthermore, the overall apparent activation energy was calculated by the following equation (36);

$$E_{ov} = E_1X_1 + E_2X_2 + \ldots\ldots + E_nX_n \qquad \text{(Equation 4)}$$

in which, X_1 to X_n are mass fractions of the content of samples reacted during each region of Arrhenius linearity. Later, Cumming used the same method to study the activation energy for a different kind of coal (40).

Galwey (41) and Garn (42) studied the ratio of E/log A which is known as the kinetic compensation effect. This effect has been reported for a number of different areas of research, particularly surface catalysis and the thermal decomposition of inorganic solids. The compensation effect occurs in a group of related reactions for which the influence of changes in A on reaction rate is offset to a greater or lesser extent by a systematic variation in E, often expressed as:

$$\log A = B + eE \qquad \text{(Equation 5)}$$

where B and e are constants. This effect has been observed in both heterogeneous and homogeneous rate processes. From E and log A values in Equation 5. The ratio of E/log A will be different for different reaction mechanisms. For the same reaction mechanisms, the ratio of E/log A will be the same. The existence of a linear relation between log A and E is considered a general characteristic. One of the possible explanations for the observed relationship between the pre-exponential factor and the activation energy for a particular series of reactions has been attributed to the use, or more accurately the abuse, of the Arrhenius equation (42).

The above analysis demonstrates that any reactions having a common on-set temperature will yield log A and E values which exhibit the kinetic compensation effect. Eliminating the possibility of a theoretical or mechanistic explanation for the compensation effect there remains the question that an artifact may be the cause of limitation of useful data. Apparently, the temperature regime in which data is collected is fairly restricted when kinetics is specifically studied by TG techniques. This is due to the data collection which is determined by the response rate of the apparatus. Very slow or very fast rates of change in weight are not studied and the range of temperature investigated is thereby limited.

The reactivity of carbon and mass transport of the reactants and products can play an important role in the kinetics of a gas-carbon reaction (43). According to Satterfield (44), three different reaction zones, i.e., chemical-control region (zone 1), pore diffusion-control region (zone 2) and film diffusion-control region (zone 3), can be observed in a solid-gas reaction (see Figure 2). At low temperature, the rate of reaction of zone 1 is relatively slow. The dominant controlling mode is chemical, i.e., the rate is governed by chemisorption of reactant and desorption of product during the carbon-gas reaction (45). With increased temperature, the rate of reaction approaches pore diffusion (zone 2) control and is, therefore, determined by the rate of mass transport of the reacting gas near the surface and that of products in the opposite direction. In other words, the desorption in zone 1 is slowly replaced by adsorption in zone 2 (43). As temperature is further increased, the rate of reaction becomes diffusion-controlled (zone 3) and thus a function of the mass of reacting gases and products transferred to and from the solid surface to the bulk gas. In zone 3, the apparent activation energy approaches zero. Here the reaction order is first order because mass-transfer is first order (44). In zone 2, the activation energy is approximately one-half of that activation energy in zone 1. According to Walker (43), the activation energy in the chemical controlled zone is the real or intrinsic activation energy. Also, the activation energy can be calculated from conversion data.

E. Cation Studies of Coal by TGA

In the case of inorganic constituents, several researchers (46,47) found the presence of ion-exchange cations (i.e., Ca^{2+} or Mg^{2+}) suppressed the evolution of volatiles during rapid pyrolysis of lignite. There is a general consensus that ion exchange cations promote secondary char-forming reactions (cracking and/or polymerization), thereby reducing volatile matter yield and changing product composition. Specific mechanisms for these reactions have not yet been determined. However, it is suggested that ion-exchange cations either react chemically with the volatile matter or prevent the escape of volatile matter molecules from coal particles by physically blocking pores which act as exit routes. It is understood (48) that the presence of cations (Na^+, K^+, Ca^{2+}) would alter relative yields of CO_2 and CO but would not affect the total amount of volatile matter evolved, nor the total amount of char. Again, they found the activation energy of the coal to have been reduced (first order Arrhenius assumed) in the presence of cations. Therefore, the presence of metal cations will affect the pyrolysis kinetics and mechanisms.

The behavior of low rank coal is believed to be greatly influenced by the inorganic constituents present which mainly contain exchangeable metal cations. American low rank coal has primarily alkali and alkaline-earth metal ions exchanged on their carboxyl groups (49). Tanabe (50) suggests that these metal ions act as polymerization catalysts for hydrocarbons. Longwell and co-workers (51) are currently investigating the effect of calcium oxide on the cracking of aromatics and other hydrocarbons. They have found that calcium oxide cracks aromatics more efficiently than it does other hydrocarbons such as aliphatics. However, the finding that coke and tar were the principal products implies that calcium oxide was selectively polymerizing rather than cracking the aromatic compounds.

Different ranks of coal have different thermal parameter values. The purpose of this research was to investigate the properties and roles of thermal parameters for coal blends under pyrolysis and combustion processes using TGA. We also wanted to determine if thermal parameters for coal blends have an additive trend under both isothermal and non-isothermal conditions. Coal blends are formed when two or more different coals are blended with different proportions. Furthermore, the thermal parameter data were used to conduct a kinetic study of coal blends. It could possibly lead to the further understanding of the properties of these coal blends and the economical utilization of these blends in the power industry.

Review of other coal studies shows that applications using TGA as an analytical method have been developed and are continuously improving in the study of coal by researchers in many countries. But investigations involving various coal blends using TGA have not yet been published. Therefore, our research not only may have a promising future in industrial utilization, but also may create a new area of basic research in the field of coal chemistry. It is of great significance both theoretically and practically.

EXPERIMENTAL

Before any samples were run, they had to undergo a certain amount of preparation. Seven coal samples and six coal blends were used for this study. It was also important to establish optimum instrumental conditions. Finally, it is important to maintain constant experimental conditions in order to get better reproducibility and also to allow for comparisons among different labs.

A. Sample Preparation

Seven coal samples of varying ranks were used in this study. The origins of the coals are given in Table 1 and analytical values for the individual coals are listed in Table 2. The concentrations of the major and minor oxides in the ash from each of the seven individual coals are listed in Table 3. The seven samples ranged in rank from medium-volatile bituminous down to lignite with the percent carbon on dry, mineral matter free basis (dmmf) in the coals ranging from 90.69% down to 69.84%. The analytical data for carbon content (dmmf) of the seven coals are given in Table 4. We used six sets of coal blends for this study made by combining two kinds of individual coal samples. The blends were prepared from air-dried samples of the coals. The six sets of binary blends were

TABLE 1

COALS USED IN BLEND STUDY

Coal No.	Rank*	Source
86027	Lig A	PRPS Coal, Saskatchewan, Can.
85091	Lig A	BDPS Coal, Saskatchewan, Can.
86039	Sub B	Jacob's Ranch Mine, Wyoming
82045	Sub C	Belle Ayr Mine, Wyoming
86046	hvAb	Poplar Lick Mine, Bell Co., Kentucky
85099	hcBb	WKy #12, Muhlenberg Co., KY
86026	mvb	Consolidation Coal Co., Pennsylvania

* Apparent rank using as-determined moisture values.

TABLE 2

ANALYTICAL VALUES FOR COALS USED IN BLENDS

	Coal Nos.			
Parameters*	86027	85091	86039	82045
% Moisture	17.95	18.39	15.24	16.04
% Ash	18.89	15.10	8.27	5.78
% Vol Mat.	41.0	39.5	44.1	43.2
% Carbon	55.31	59.42	66.78	67.95
% Hydrogen	3.33	3.57	4.60	4.22
% Nitrogen	.38	.96	.97	.93
% Sulfur	.73	.34	.64	.36
Btu/lb	8,767	9,612	11,434	11,340
HGI	35	34	40	41
FSI	0	0	0	0

TABLE 2 (contiuned)

	Coal Nos.		
Parameter*	86046	85099	86026
% Moisture	2.03	5.92	1.07
% Ash	10.81	15.15	6.03
% Vol Matter	38.4	35.7	25.3
% Carbon	73.87	64.55	84.36
% Hydrogen	5.06	4.03	4.55
% Nitrogen	1.57	1.37	1.08
% Sulfur	.89	3.78	.85
Btu/lb	13,186	11,421	14,668
HGI	40	50	90
FSI	4.0	1.0	9.0

* Moisture is as-determined; all other analyses are reported on a dry basis.

TABLE 3

ELEMENTAL COMPOSITION OF ASHES FROM COALS USED IN BLENDS

	Coal Nos.			
Metal Oxide	86027	85091	86039	82045
% SiO_2	41.14	44.88	35.47	33.05
% P_2O_5	0.63	0.45	1.31	1.50
% SO_3	7.84	5.66	10.54	9.26
% K_2O	1.60	1.02	0.48	0.16
% CaO	13.21	13.15	18.48	26.9
% TiO_2	0.82	1.07	1.12	1.25
% Fe_2O_3	4.20	3.49	6.25	5.57
% Na_2O	0.92	0.72	1.20	1.04
% MgO	1.40	1.20	3.27	4.59
% Al_2O_3	23.16	21.36	16.69	14.70

TABLE 3 (continued)

	Coal Nos.		
Metal Oxide	86046	85099	86026
% SiO_2	50.43	45.47	8.62
% P_2O_5	2.36	0.20	0.01
% SO_3	1.08	0.72	7.99
% K_2O	1.91	2.63	1.34
% CaO	2.71	0.55	9.26
% TiO_2	1.66	1.00	1.18
% Fe_2O_3	5.32	24.14	12.25
% Na_2O	0.63	0.51	0.79
% MgO	1.06	1.07	1.61
% Al_2O_3	24.51	19.22	24.72

TABLE 4

CARBON PERCENTAGE FOR SEVEN DIFFERENT RANKS OF COAL SAMPLES

WKU Coal Sample No.	Coal Rank	Carbon Content (dmmf) (%)
86026	Medium Volatile Bituminous 1(MV1)	90.69
86046	High Volatile Bituminous 1 (HV1)	84.10
85099	High Volatile Bituminous 2 (HV2)	79.15
86039	Subbituminous 1 (Sub1)	73.61
82045	Subbituminous 2 (Sub2)	72.63
85091	Lignite 2 (lig2)	71.16
86027	Lignite 1 (Lig1)	69.84

prepared from -8 mesh (2.4 mm) samples of each coal. In each set, four blends (80:20, 60:40, 40:60, and 20:80) of the two coals were then prepared by thoroughly mixing the appropriate weights of each coal. The six sets of combination of coals used for binary blends are shown in Table 5. In preparing each blend, care was taken so that the smallest quantity of each coal used was never less than 1000 g. This was done so that a representative sample of each coal was maintained for the blend preparation and analysis. The total number of blends prepared in this series was 24 (six sets x 4 blends). After mixing, the blends were split and a 1000 g subsample was pulverized to -60 mesh (250 u) for all coal samples and their blends resulting in the samples we used for testing. All coal samples and blends were prepared and analyzed by Fred Hayes, Mark Risen and Dr. John T. Riley in the Coal and Fuel Characterization Laboratory at Western Kentucky University.

B. Instrumental Operation

The experiments were performed on a thermogravimetric analyzer (TGA) using the temperature programming mode. The temperature programming mode has frequently been used to understand the characteristics of coal pyrolysis and combustion because the experiments are required to cover the whole temperature range of decomposition (20,36,52). The survey instrument is a DuPont 951 Thermogravimetric Analyzer connected to a DuPont 1090B Thermal Analyzer and a DuPont 1091 Disk System.

TABLE 5

COMBINATIONS OF COALS USED FOR BINARY BLENDS

Blend	Combination
1	2 lignites (86027 + 85091)
2	lignite + subbit. (86027 + 86039)
3	2 subbit. (86039 + 82045)
4	subbit. + high vol. bit. (86039 + 86046)
5	2 high vol. bit. (86046 + 85099)
6	high vol. bit. + med. vol. bit. (86046 + 86026)

The analytical procedure for studying the decomposition of coal and coal blends was as follows. About 10 mg of coal sample or coal blend was placed in a platinum sample pan with a microbalance and heated to decomposition employing a temperature programmed furnace. For non-isothermal combustion or pyrolysis conditions, the sample was heated at 20 °C/min from 30 °C to a maximum temperature of 750 °C for combustion or 1000 °C for pyrolysis. For isothermal combustion conditions, the samples were heated at a constant temperature. In order to investigate the break point of each sample, we chose different isothermal temperatures for different ranks of coal blends so that the results could show the break points and combustion end points for all samples during the heating process. For example, we set up 600°C for MV1 and HV1 coal blends, 550°C for HV1 and HV2, HV1 and Sub1 coal blends, and 400°C for Sub1 and Sub2; Sub1 and Lig1; Lig1 and Lig2 coal blends. In these cases, if we use 600°C for all samples, the low rank coal blends would decompose so fast that the break points could not be observed. On the other hand, if we use 400°C for all samples, the high rank coal blends could not decompose completely under such a low temperature so that the combustion end points could not be observed. For isothermal combustion process, as soon as the isothermal temperature was reached, the sample pan was introduced into the isothermal furnace and heated for 30 min.

The flow rate of nitrogen (pyrolysis) or air (combustion) was set at 50 ml/min, measured at room temperature (about 20

°C). Throughout the isothermal and programmed heating process, the time was read every eight seconds, and the temperature of the coal blend on the sample pan was determined by the thermal detector while the weight loss was determined by the microbalance. From the plots of mass loss vs. temperature (non-isothermal conditions) or time (isothermal conditions) recorded during the experiments, several thermal parameter values, such as T_{max}, R_{max}, T_i, weight loss, $T_{1/2}$, residue, t_{max}, $t_{break\ point}$ and $t_{combustion\ end\ point}$ can be determined.

C. Experimental Technique

The results of thermal studies might sometimes be difficult to reproduce because of the variations in experimental conditions used. TG and DTG curves will be affected by instrumental factors such as heating rate, flow rate, and sample holder, and sample characteristic factors such as sample mass and sample particle size (20,52). For this research, we maintained the same sample weight (about 10 mg), the same heating rate for non-isothermal processes (20 °C/min), the same particle sizes, the same shape for the sample holder and the same method of loading for a series of samples. It was very important in this research that the same experimental conditions were maintained throughout the course of the work. Changing the position of the thermal detector and the sample pan slightly would cause significant changes in the thermal parameter values. The triangular shape of the sample pan also had to be maintained at all times.

In order to avoid establishing a thermal gradient in the sample, all samples were spread evenly on the platinum pan which is triangular in shape. For non-isothermal pyrolysis conditions, as soon as the sample was introduced into the furnace, the instrument started to record and heat to the initial temperature of 30 °C. The system was held at approximately 30 °C for 5 minutes in the pyrolysis runs, which was sufficient time for the furnace to be purged of all air. We then heated at the programmed heating rate to the desired final isothermal temperature of 1000 °C. The sample was held at 1000 °C for 2 minutes in order to allow the sample and furnace temperatures time to equilibrate. The thermogram was recorded throughout the run (even during the isothermal step). The weight percent control was set at 100% full scale deflection on the recorder chart, and the microprocessor start button is pressed. This unit controls all the automatic functions of the recorder, as well as the temperature programmed furnace.

RESULTS AND DISCUSSION

For this research, all seven individual coal samples and their blends were used. The samples were exposed to two different atmospheres--nitrogen (pyrolysis) and air (combustion) in order to better understand the pyrolysis and combustion behavior of coal.

A. Pyrolysis Behavior of Coal Blends

It is important to determine whether or not the samples being used are homogeneous and also to determine the optimum sample size for the maximum reproducibility. This section will discuss sample homogeneity and reproducibility. Furthermore, we will focus on pyrolysis behavior of coal blends under non-isothermal conditions.

1. TG Curves

Typical thermogravimetric heating curves (TG curves) for two individual coal samples under non-isothermal conditions in nitrogen are shown in Figures 1 and 3. Figure 1 is the thermogram for a high volatile bituminous coal (HV1) and Figure 3 is for a subbituminous coal (Sub1). Two different thermodecompostion stages are observed for all the coal samples which are represented by the two peaks on the DTG

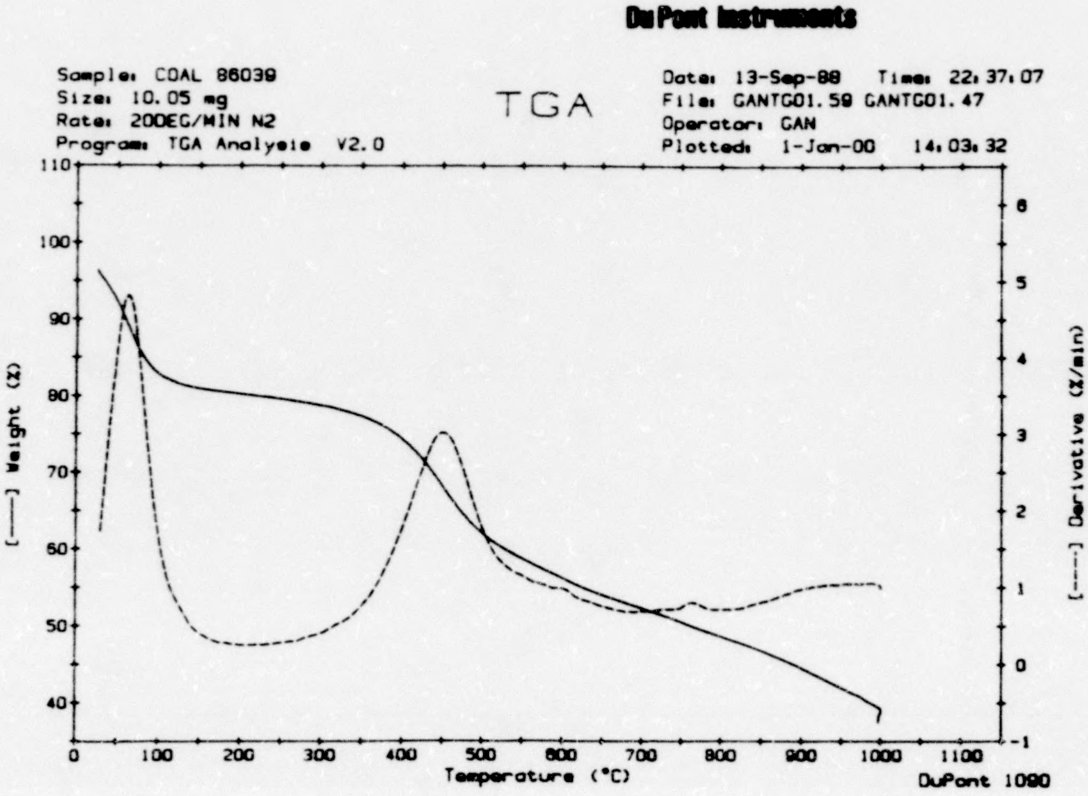

Figure 3. TG Heating Curve - Subl Coal in Nitrogen under Non-isothermal Conditions.

curve. For simplicity, these two decompositions will be labelled zone 1 and zone 2 for all coal and coal blend samples discussed in this thesis. Zone 1, the first thermodecomposition stage, which is present around 80 °C is due to the loss of inherent moisture. Zone 2, the second thermodecomposition stage, is present about 460 °C, and is due to the volatile matter being released. Further decomposition occurred at a relatively constant weight-loss rate until the final set temperature of 1000 °C was reached.

The values of five important kinetic parameters that were studied related to zone 2.

(1) T_i (°C), the temperature at which the rate of weight-loss reached to 1.00%/min;

(2) T_{max} (°C), the temperature at which the maximum rate of weight-loss occurred;

(3) R_{max} (%/min^{-1}), the reactivity at T_{max}, this value equaled to the maximum rate of weight-loss;

(4) $T_{1/2}$ (°C), the temperature at 50% conversion of the weight loss which was measured from where the volatile matter started to be released (around 220°C) until the rate of weight-loss (dm/dt) remained constant (around 1000°C);

(5) volatile matter (%), the relative weight loss on a dry basis within zone 2.

These kinetic parameters were measured under the following conditions. First, for higher rank coals (medium-volatile and high-volatile bituminous coals), the relative weight loss (%) on a dry basis within zone 2 was measured for the interval of 220 °C to 1000 °C. Second, for lower rank coals (subbituminous and lignite coals), the relative weight loss (%) on a dry basis within zone 2 was measured for the interval of 220 °C to 910 °C. This was done because we observed that the rate of mass loss (dm/dt) for low rank coals was constant around 910°C and started to change after 910°C. Using thermograms such as those in Figures 1 and 3, we obtained the five parameter values listed in Table 6.

To compare the difference between a high volatile bituminous coal and a subbituminous coal under pyrolysis conditions using Figures 1 and 3 and the data of Table 6, we found that the appearance of TG and DTG curves of these two samples were similar but all five thermal parameters were different. Higher rank coals seemed to have higher T_{max}, R_{max}, and T_i values but lower volatile matter and $T_{1/2}$ values. Further studies were done to determine trends for these parameters for a series of coal samples with ranks varying from medium volatile bituminous to lignite.

2. Sample Size

We know that coal samples are not homogeneous and a large sample weight might provide a more representative sample. However, it would also have produced more effluent gases that could impede the progress of the volatilization reactions. Furthermore, the sample pan was small, so it would establish a thermal gradient if the sample could not be spread evenly on the platinum pan. Therefore, 10 mg was chosen as the

TABLE 6

FIVE PARAMETER VALUES FOR TWO INDIVIDUAL COAL SAMPLES AND THEIR BLEND DURING NON-ISOTHERMAL PYROLYSIS

Coal Sample	T_{max} (°C)	R_{max} (%/min)	T_i (°C)	Volatile Matter (%)	$T_{1/2}$ (°C)
HV1	463.7	5.98	398.6	37.69	479.5
40%Sub1+60%HV1	459.1	4.96	384.2	40.59	492.1
Sub1	449.9	3.03	366.4	45.00	526.7

maximum sample size since this size of coal sample allowed even spreading on the pan without establishing a thermal gradient (53).

Before we ran all the samples, we decided to test the sample size to determine the optimum sample size to achieve maximum repeatability. We made numerous runs for three different sample sizes-- 2.5 mg, 5 mg, and 10 mg. We used a high-volatile bituminous coal under non-isothermal pyrolysis conditions in nitrogen to study the repeatability of the technique by determining if the same results were obtained for the three different sample sizes chosen. Three thermal parameters-- T_{max}, R_{max}, and volatile matter (dry basis)-- were considered and the results are illustrated by Figures 4-6. The T_{max} values for 2.5 mg and 5 mg were partially out of the 95% confidence interval for the mean which was determined by the 10 mg samples (Figure 4). The R_{max} and volatile matter (dry basis) for 2.5 and 5 mg were totally out of the 95% confidence interval for the 10 mg mean (Figures 5 and 6). Thus, if we used either 5 mg or 2.5 mg as the sample size, we would have a higher degree of error in our thermal parameter measurements. In general, 10 mg was the best choice for the sample size for all subsequent runs.

3. Repeatability

After we established the optimum sample size, we wished to test the sample for repeatability to determine the deviation ranges and accuracy of the experiments. We ran 6

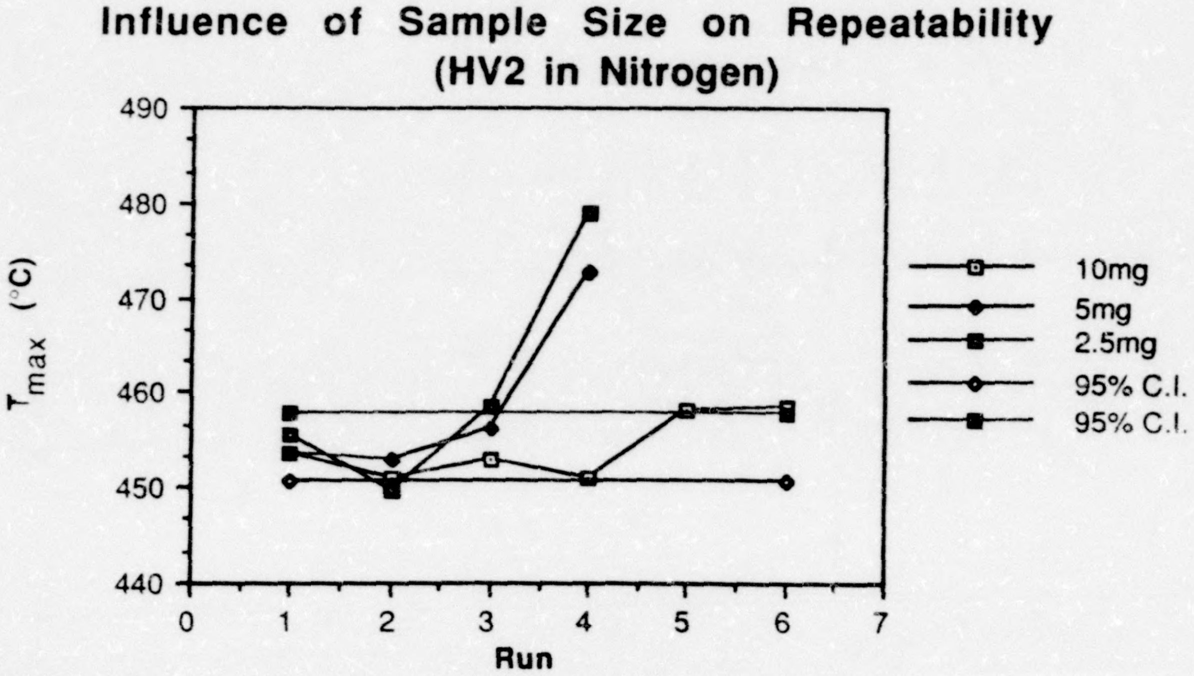

Figure 4. Influence of Sample Size on Repeatability - T_{max} for HV2 Coal in Nitrogen under Non-isothermal Conditions.

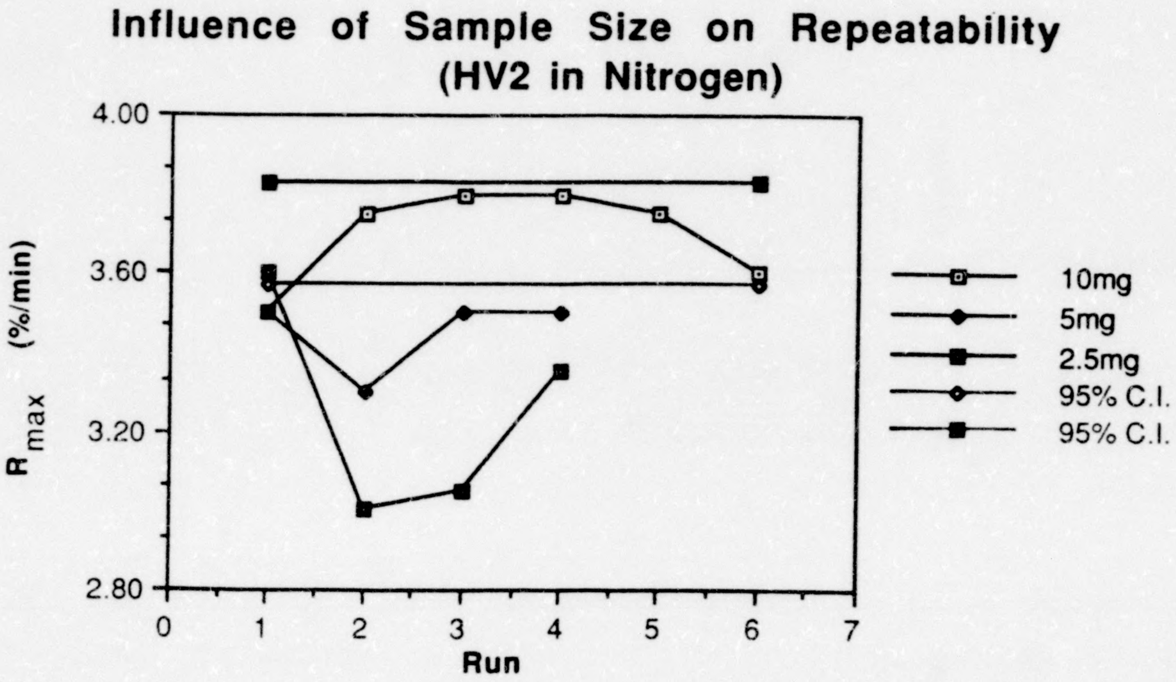

Figure 5. Influence of Sample Size on Repeatability - R_{max} for HV2 Coal in Nitrogen under Non-isothermal Conditions.

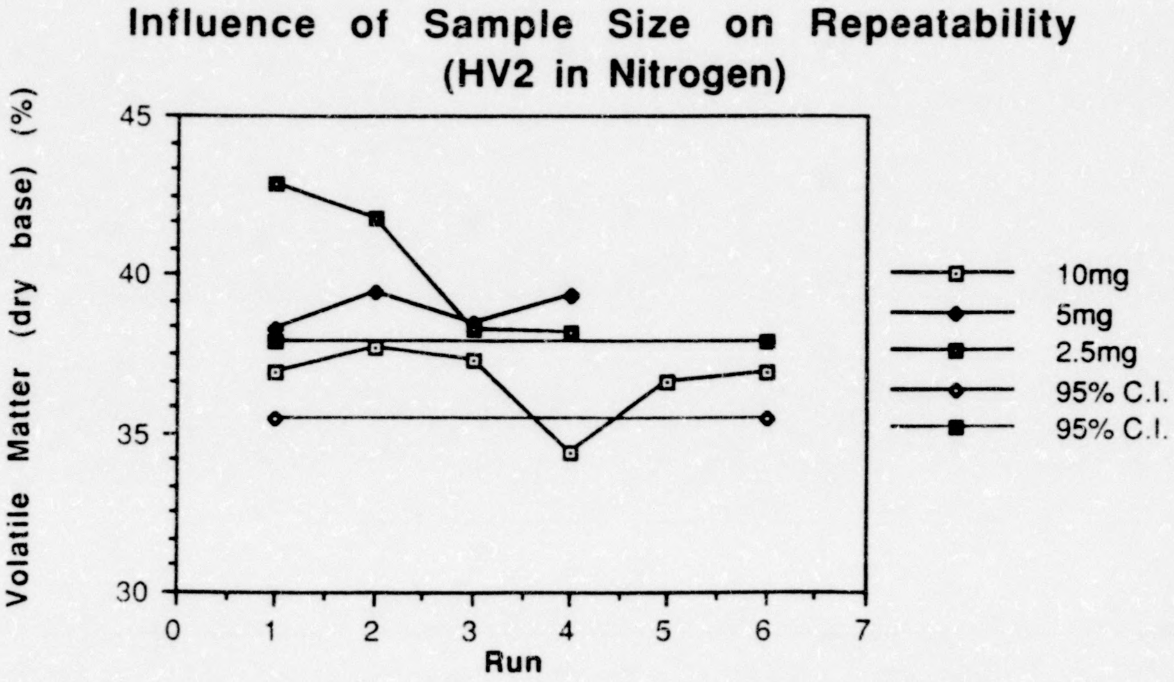

Figure 6. Influence of Sample Size on Repeatability - Volatile Matter for HV2 Coal in Nitrogen under Non-isothermal Conditions.

trials on each of the 7 individual coal samples, using 10 mg samples under non-isothermal pyrolysis conditions in nitrogen. The relative standard deviations of T_i, T_{max}, $T_{1/2}$, R_{max} and volatile matter for these 7 coal samples are listed in Table 7. From Table 7, the largest relative standard deviations of the parameters of temperature such as T_i, T_{max}, $T_{1/2}$ were 2.2%, 1.5% and 3.0%, respectively. They were produced by lignite coal 1 (carbon content of 69.84%), subbituminous coal 2 (carbon content of 72.63%) and subbituminous coal 1 (carbon content of 73.61%) (Figures 7-9); The average relative standard deviations of T_i, T_{max}, and $T_{1/2}$ were 1.3%, 1.1%, and 1.9% (Figures 7-9). the largest relative standard deviation of the parameters of weight such as R_{max} and volatile matter were 3.2% and 4.0%, which were produced by lignite coal 1 (carbon content of 69.84%) and subbituminous coal 2 (carbon content of 72.63%) (see Figures 10-11). The average relative standard deviations of R_{max} and volatile matter were 3.2% and 2.9% (Figures 10-11). There is no apparent trend such as the increase in relative standard deviation with a corresponding decrease in coal rank. However, the relative standard deviation values of lower rank coals (lignite or subbituminous) were generally greater than those of higher rank coals (medium or high volatile bituminous). The five thermal parameters studied resulted in similar values for all runs with a sample mass of 10 mg, which is the reason we chose 10 mg as our most repeatable sample size. All subsequent runs for pyrolysis and combustion used a sample size of 10 mg.

TABLE 7

RELATIVE STANDARD DEVIATIONS OF PARAMETERS OF INDIVIDUAL COALS

	Relative Standard Deviations (%)				
Coal Samples	T_{max}	R_{max}	T_i	Volatile Matter	$T_{1/2}$
MV1	0.54	2.4	0.76	3.8	0.8
HV1	0.92	2.8	1.2	1.2	1.3
HV2	0.75	3.2	0.97	3.1	0.8
Sub1	1.2	3.3	1.5	3.6	2.9
Sub2	1.3	4.0	2.2	3.2	2.3
Lig2	1.4	3.7	1.1	1.4	3.0
Lig1	1.5	3.0	1.1	4.0	2.4

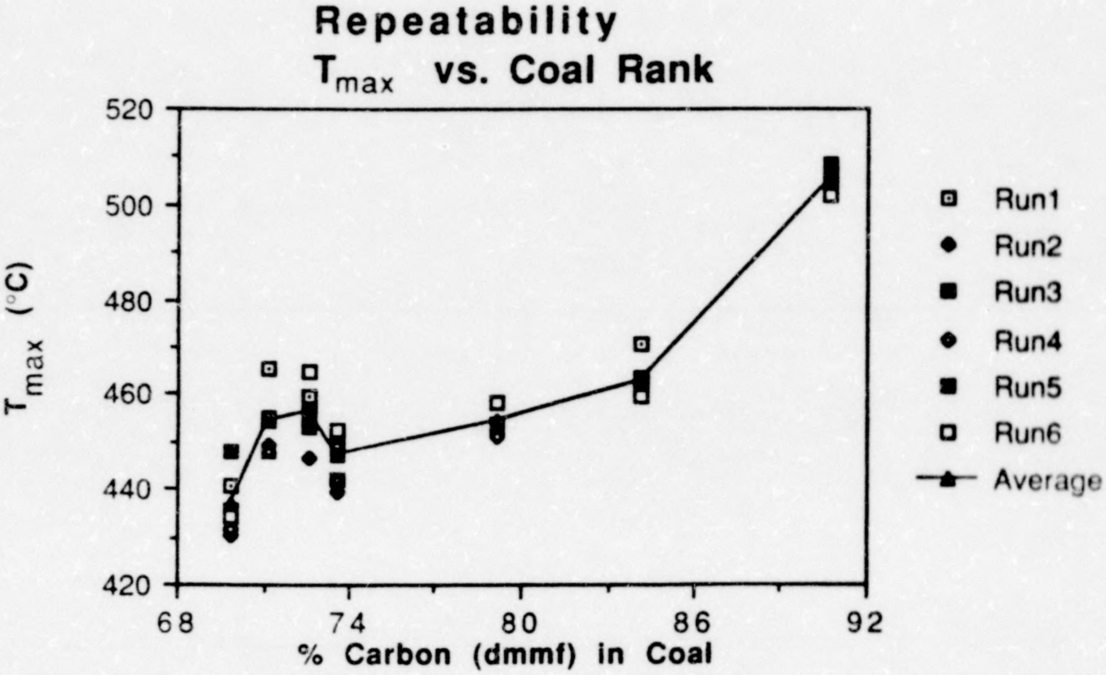

Figure 7. Repeatability of T_i for Seven Coal Samples with Different Carbon Contents.

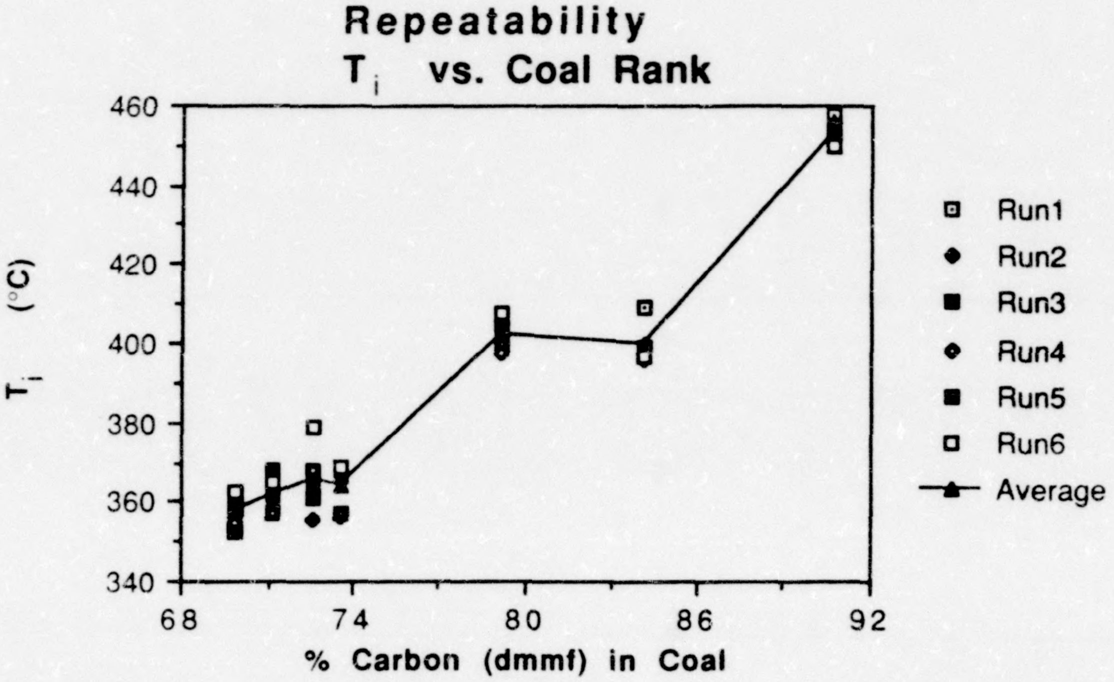

Figure 8. Repeatability of T_i for Seven Coal Samples with Different Carbon Contents.

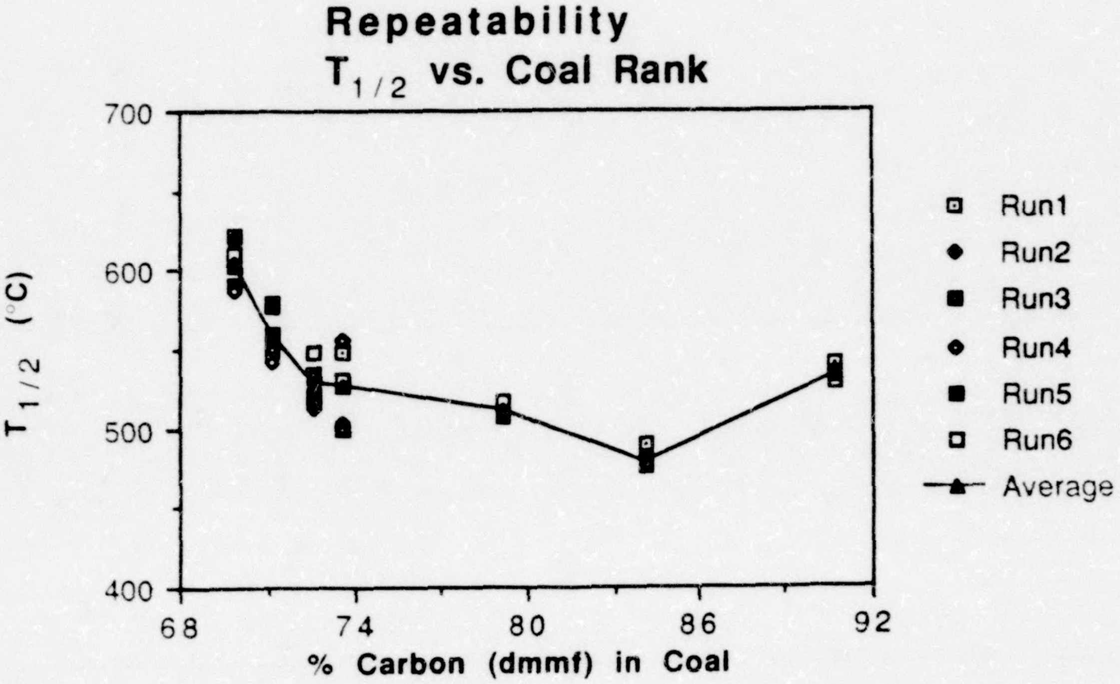

Figure 9. Repeatability of $T_{\frac{1}{2}}$ for Seven Coal Samples with Different Carbon Contents.

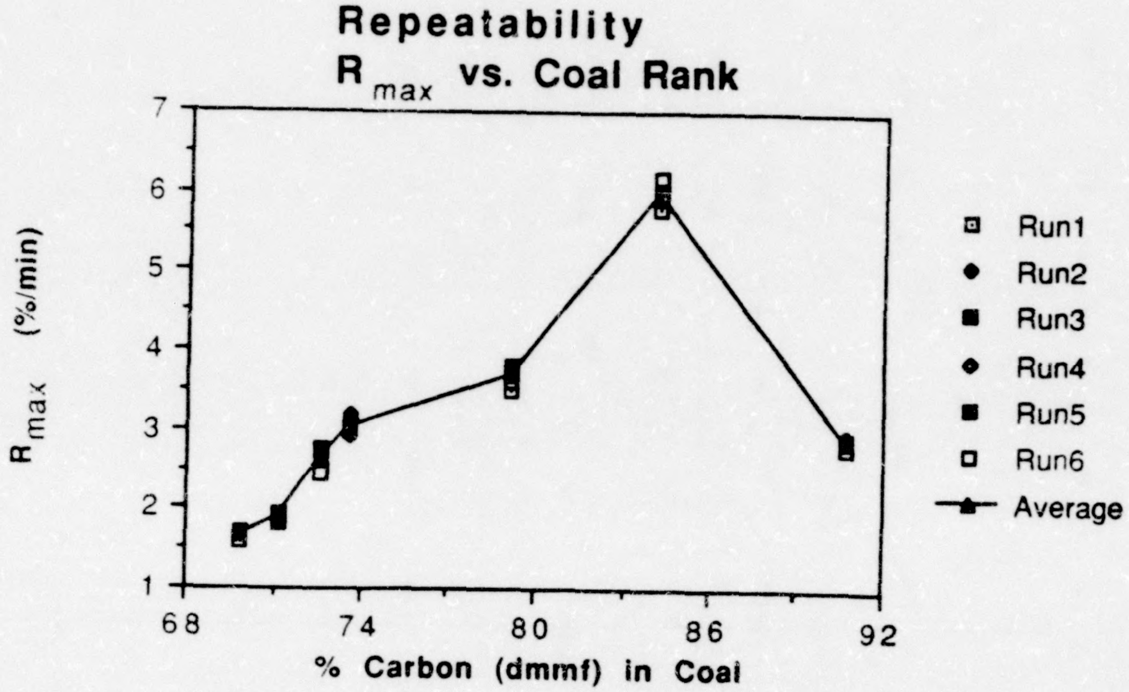

Figure 10. Repeatability of R_{max} for Seven Coal Samples with Different Carbon Contents.

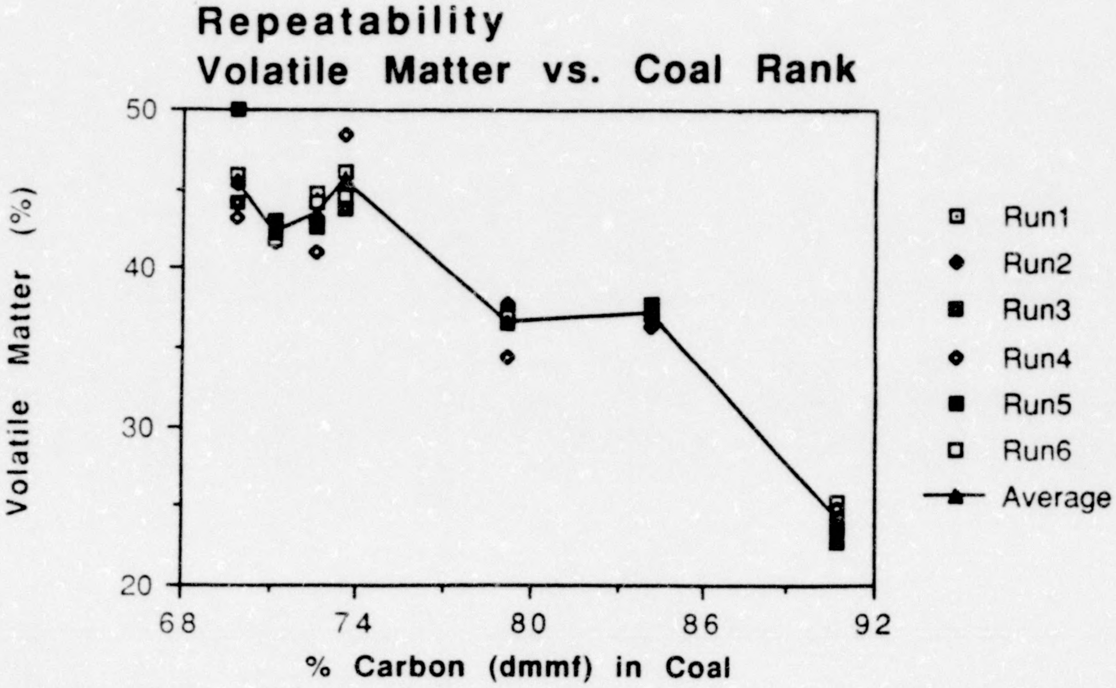

Figure 11. Repeatability of Volatile Matter for Seven Coal Samples with Different Carbon Contents.

Next we considered the relationships between coal rank and TGA parameters. All values for the five TGA parameters ranging in rank from medium volatile bituminous 1 to lignite 1 are presented in Table 8. The data obtained gave the following results. First, when coal rank increased, T_i increased from 358.1 °C (lignite 1) to 452.9 °C (medium volatile bituminous 1) (Figure 7). This is because the decomposition reaction of a low rank coal will be easier to start than that of a high rank coal. Second, T_{max} increased from 436.8 °C (lignite 1) to 504.9 °C (medium volatile bituminous 1) (Figure 8). This is because low rank coals will decompose and reach the maximum rate of release of volatile matter faster than the high rank coals. T_i and T_{max} gave similar results in that both increase when the coal rank increases. Therefore, in regards to kinetic results, the T_i and T_{max} show a similar trend. Third, R_{max} increased from 1.66%/min (lignite 1) to 6.00%/min (high volatile bituminous 1) and then down to 2.86%/min (medium volatile bituminous 1) (Figure 10). Previous work has shown the dependence of burning profiles (pyrolysis + loss of fixed carbon) on differences in coal rank (23,54,55). These studies indicated that the maximum value of R_{max} (%/min) was within the bituminous coal range but not within the subbituminous or the anthracite coal ranges. Fourth, $T_{1/2}$ tended to decrease from 605.1 °C (lignite 1) to 478.9 °C (high volatile bituminous 1) then increase to 532.7 °C (medium volatile bituminous 1) (Figure 9). This behavior agrees well with the results for R_{max}, but in an

TABLE 8

VALUES OF FIVE PARAMETERS FOR SEVEN INDIVIDUAL COALS

Coal Samples	Average values of six runs				
	T_{max} (°C)	R_{max} (%/min)	T_i (°C)	Volatile Matter(%)	$T_{1/2}$ (°C)
MV1	504.9	2.86	452.9	24.23	532.7
HV1	462.7	6.00	399.8	37.20	478.9
HV2	454.3	3.70	402.1	36.64	511.8
Sub1	447.1	3.03	363.9	45.49	527.1
Sub2	456.4	2.66	365.8	43.30	527.6
Lig2	454.6	1.88	362.0	42.26	558.8
Lig1	436.8	1.66	358.1	45.56	605.1

inverse manner. Therefore, if R_{max} has a high value then $T_{1/2}$ will have a low value, and vice versa. The reason for this inverse relationship is that an increase in R_{max} corresponds to an increase in reactivity which will lower the $T_{1/2}$ value. Fifth, weight loss (W.L.) on a dry basis represented by the second peak of the DTG curve agrees well with volatile matter of coals. Weight loss for the seven coals decreased from 45.44% (lignite 1) to 24.23% (medium volatile bituminous 1). The values of the TGA volatile matter were almost the same as those obtained using the ASTM method (Figures 11 and 12). From these two figures one can see that high rank coals have lower volatile matter values than low rank coals.

Riley and co-workers (14) employed ASTM method D3175 to obtain a group of volatile matter data (dry basis) for coal blends, and reported a nonadditive relationship between the determined volatile matter and that calculated from a weighted average of that from the coals used to make the blends. We wanted to compare the volatile matter values of coal blends obtained from ASTM and from TGA. Last, using MV1 and HV1 coal blends as an example, we compared the TGA volatile matter and the ASTM D3175 volatile matter values for the coal blends. These two coals were chosen because the difference between the volatile matter values for the MV1 and HV1 coals was the largest among those coals used in the study. Table 9 lists the volatile matter values determined for MV1 and HV1 blends. For comparison, the TGA and ASTM volatile matter values were plotted on Figure 13. The values and trends obtained from

TABLE 9

COMPARISON OF VOLATILE MATTER RESULTS FROM TGA AND ASTM METHOD

Coal Blends %MV1/%HV1	TGA Volatile Matter (dry basis)(%)	ASTM D3175 Volatile Matter (dry basis)(%)
0%MV1/100%HV1	37.20	37.86
20%MV1/80%HV1	34.55	35.94
40%MV1/60%HV1	32.64	33.14
60%MV1/40%HV1	30.47	30.90
80%MV1/20%HV1	27.21	27.76
100%MV1/0%HV1	24.23	24.27

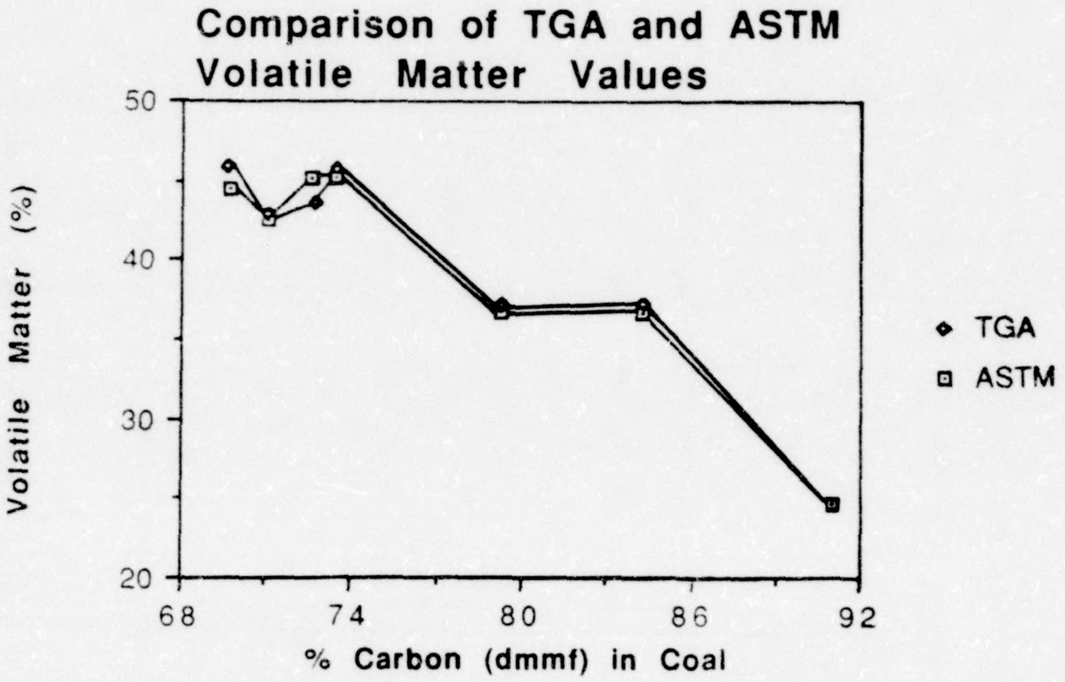

Figure 12. Comparison of Volatile Matter from TGA and Volatile Matter from ASTM Method. (Individual Coal Samples)

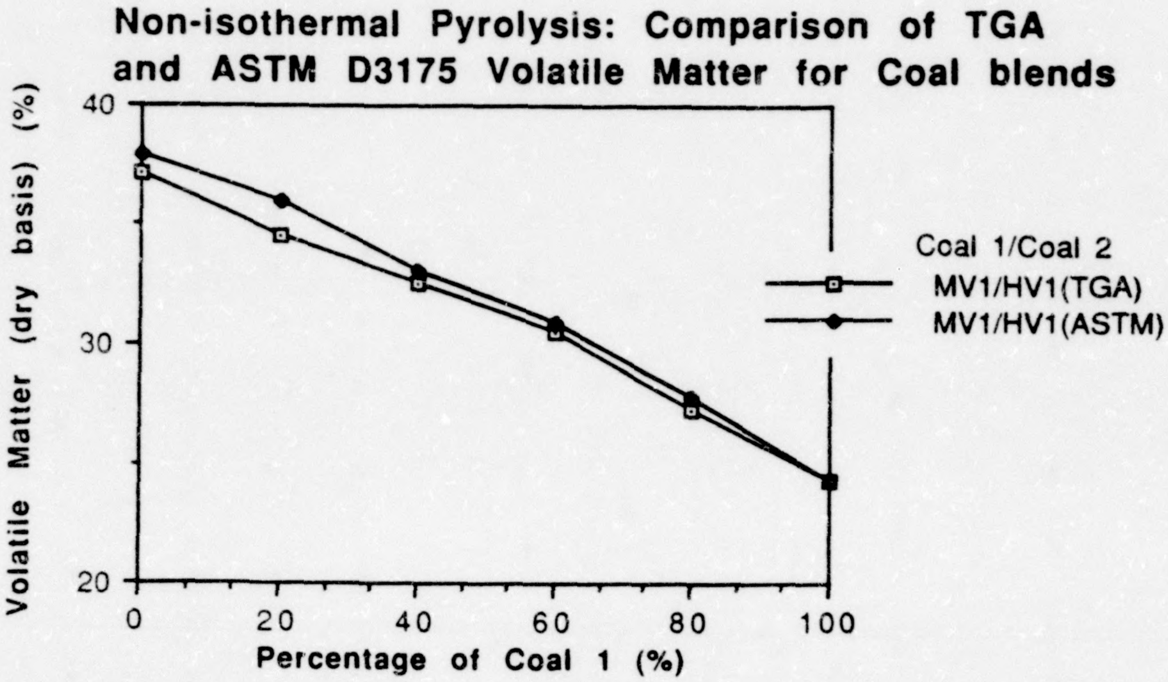

Figure 13. Comparison of TGA and ASTM D3175 Volatile Matter Values for Coal Blends.

TGA were almost the same as those from the ASTM method, which were described as nonadditive (14).

For this research, we wanted to determine whether or not the kinetic properties of coal blends are additive or nonadditive. Multiple runs were done on the individual coal samples, and we believe the average values obtained for each parameter of the individual coals are accurate. If the additive relationship is considered, the analytical values found for the various coal blends would be the same, within experimental error, as those calculated using the weighted averages of the analytical values for the individual coals. In other words, the parameter values for the two individual coals and those of their blends should form a straight line, within experimental error, if graphed. The allowed instrumental errors were determined by sample repeatability tests. The maximum relative standard deviations for pyrolysis parameters determined on six runs for the seven individual coals are shown in Table 7. The experimental errors were assumed to be the same for all the measurements of temperature, weight, or time. A summary of the maximum relative standard deviations for most parameters of individual coal samples under pyrolysis and combustion conditions are shown in Table 10. The results indicate that the maximum relative standard deviations for temperature, weight, and time measurements are 3%, 4%, and 5.6%, respectively. These maximum relative standard deviations were used as the allowed maximum relative errors in this study for the determination of

TABLE 10

MAXIMUM RELATIVE STANDARD DEVIATIONS FOR ALL PARAMETERS

		Maximum Relative Standard Deviations (%)
Temperature:		
Pyrolysis Parameters		
	T_{max}	1.5
	T_i	2.2
	$T_{1/2}$	3.0
Combustion Parameters		
	T_{max}	1.9
	T_i	2.3
Weight:		
Pyrolysis Parameters		
	R_{max}	4.0
	Weight Loss	4.0
Combustion Parameters		
	R_{max}	3.9
	Weight Loss	2.0
	Residue	3.7
Time:		
Combustion Parameters		
	t_{max}	5.6
	$t_{break\ point}$	3.7
	$t_{combustion\ end\ point}$	2.0

additive or nonadditive relationships.

For example, in the case of parameters such as T_{max}, T_i and $T_{1/2}$, since repeatability tests show that the maximum relative deviation values of T_{max}, T_i and $T_{1/2}$ are 3%, the allowed maximum relative error for determination of temperature was assumed to be within ±3%. Therefore, we ran the samples of coal blends one time under the best experimental conditions. If all the experimental data was within the range of ±3%, the relationship was assumed to be additive. If the data fells outside this allowed error range, the experiments were repeated several times and the average calculated. For the average value, when the relative error between the average experimental and theoretical values was less than ±3%, an additive relationship is implied. Outside this range a nonadditive relationship is implied.

On the other hand, during the experimental process, temperature and weight are recorded every eight seconds (0.14 minute). The interval of two neighbor time values recorded is 0.14 minute. Therefore, instrumental accuracy for time is assumed to be 0.14 minute. The 0.14 minute error was allowed for time values because the instrument can not indicate the difference of time values below 0.14 minute.

4. Non-isothermal Conditions

After we tested the optimum sample and technique repeatability, we started a study of the properties of coal blends during pyrolysis. Pyrolysis decomposition involves a chemical change when a sample is heated in the presence of pure nitrogen. Figure 14 shows the TG heating curve for the coal blend of 40% Sub1 + 60% HV1. This curve shows no gross differences from the TG heating curves for the two individual coals (Figures 1 and 3) and appears to be a combination of the two. The five thermal parameters of this coal blend were shown in Table 6.

According to the maximum allowed relative errors for the measurements of temperature or weight, an additive or a nonadditive relationship can be determined for the five parameters in pyrolysis conditions. For example, the differences in T_i between the measured and weighted average values for MV1/HV1 coal blends are reported in Table 11. From this table, a nonadditive nature can be implied since the relative error is larger than 3%.

In general, for coal blends, if two individual coal samples showed very different parameters (T_{max}, R_{max}, T_i, weight loss between 220 °C and 700 °C, and $T_{1/2}$), then a nonadditive or an additive relationship could be indicated for the parameters of their blends. If two individual coal samples had similar parameter values, then inconclusive results would be indicated for the parameter values of their blends. This would imply that nonadditive relationships only developed in blends from coals with widely differing parameters. If two parameter values were very close, one could say nothing about the additive or nonadditive relationship.

A check for additivity or nonadditivity of the five

TABLE 11

COMPARISON OF T_i RESULTS FROM EXPERIMENTS AND CALCULATIONS

Coal Blends	T_i (°C)		Relative Error(%)
MV1/HV1	Experimental	Theoretical	
0%/100%	396.5	396.5	
20%/80%	402.8	407.2	1.0%
40%/60%	408.0	417.9	2.0%
60%/40%	413.5	428.5	3.5%
80%/20%	423.7	439.2	3.5%
100%/0%	449.9	449.9	

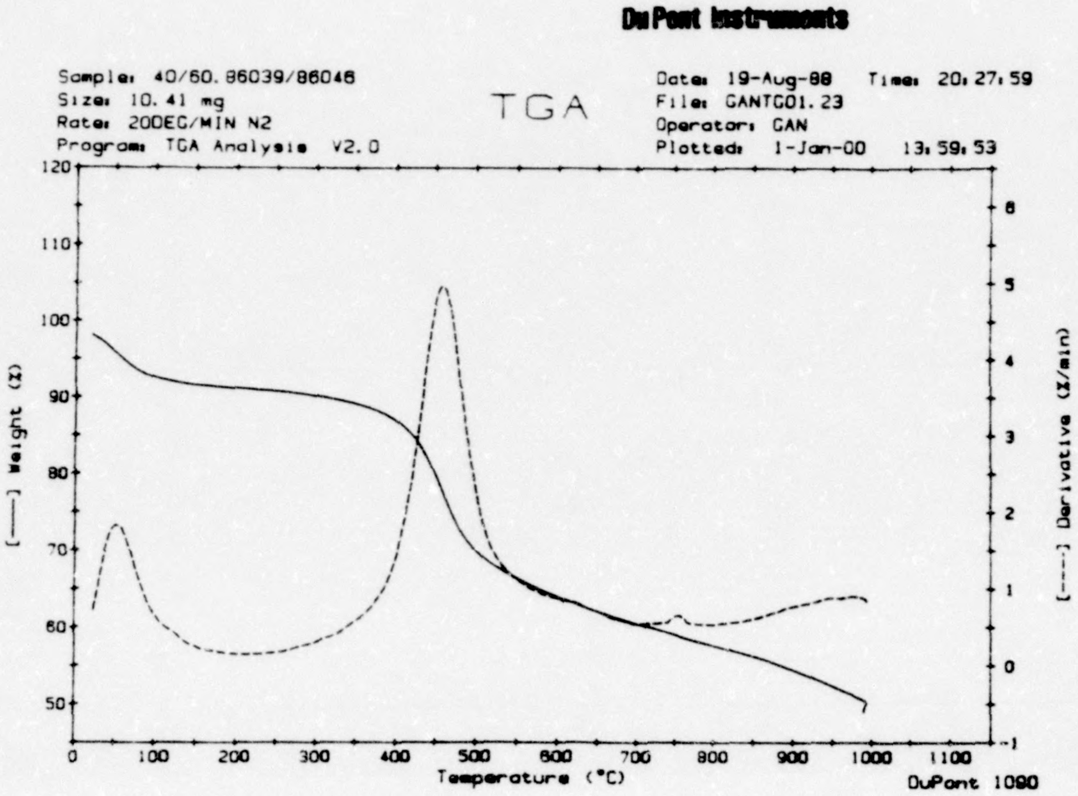

Figure 14. TG Heating Curve - The 40% Subl + 60% HVl Coal Blend in Nitrogen under Non-isothermal Conditions.

thermal parameters for the coal blends listed in Table 12 gave the results discussed in the following sections.

a. T_i - 1%/min Weight Loss Temperature

As shown in Figure 15, the values of T_i for coal blends MV1/HV1 appear to be nonadditive. When the MV1 content increased from 0% to 100%, T_i increased from 396.5 °C to 449.9 °C. The nonadditive relationship was clear because the T_i values for the MV1 and HV1 blends do not lie on a straight line. A possible explanation is that some mineral matter such as K, Ca, or Na compounds have a catalytic effect in the pyrolysis process (46,47,49-51). Different kinds of coals have different mineral matter components and different catalytic mechanisms; therefore, the nonadditive nature of the sample may be due to the mixed catalysts effect (synergism) (56). In the case of MV1/HV1 mixtures, the experimental values were lower than calculated values. The values of T_i for the Lig2/Lig1, HV2/HV1, HV1/Sub1, Sub2/Sub1, and Sub1/Lig1 coal blends do not give conclusive evidence about a nonadditive relationship. For example, for Sub1 and Lig1 coal blends, when Sub1 content increased from 0% to 100%, T_i kept almost constant within the range between 377.5 °C and 381.2 °C (Figure 15). It is hard to judge whether or not there is an additive relationship within such a small temperature range.

b. T_{max}-Temperature of Maximum Rate of Weight Loss

The values of T_{max} for coal blends MV1/HV1 appeared to be nonadditive, as shown in Figure 16. In the case of the MV1/HV1 mixture, T_{max} increased from 460.6 °C to 501.7

TABLE 12

RELATIONSHIP OF PARAMETER VALUES FOR EACH SET OF COAL BLENDS UNDER NON-ISOTHERMAL PYROLYSIS CONDITIONS

	Relationship Appears		
Parameters	Additive	Nonadditive	Inconclusive
T_i		MV1/HV1	Sub1/HV1, Lig2/Lig1 Sub2/Sub1, HV2/HV1 Lig1/Sub1
T_{max}		MV1/HV1	Sub1/HV1, Sub2/Sub1 Lig1/Sub1,HV2/HV1 Lig2/Lig1
$T_{1/2}$		MV1/HV1 Sub2/Sub1 Sub1/HV1	Lig2/Lig1, HV2/HV1 Lig1/Sub1
R_{max}		MV1/HV1 HV2/HV1 Sub1/HV1 Lig1/Sub1	Lig2/Lig1,Sub2/Sub1
Weight loss	MV1/HV1 Lig1/Sub1		Sub1/HV1, Lig2/Lig1 HV2/HV1, Sub2/Sub1

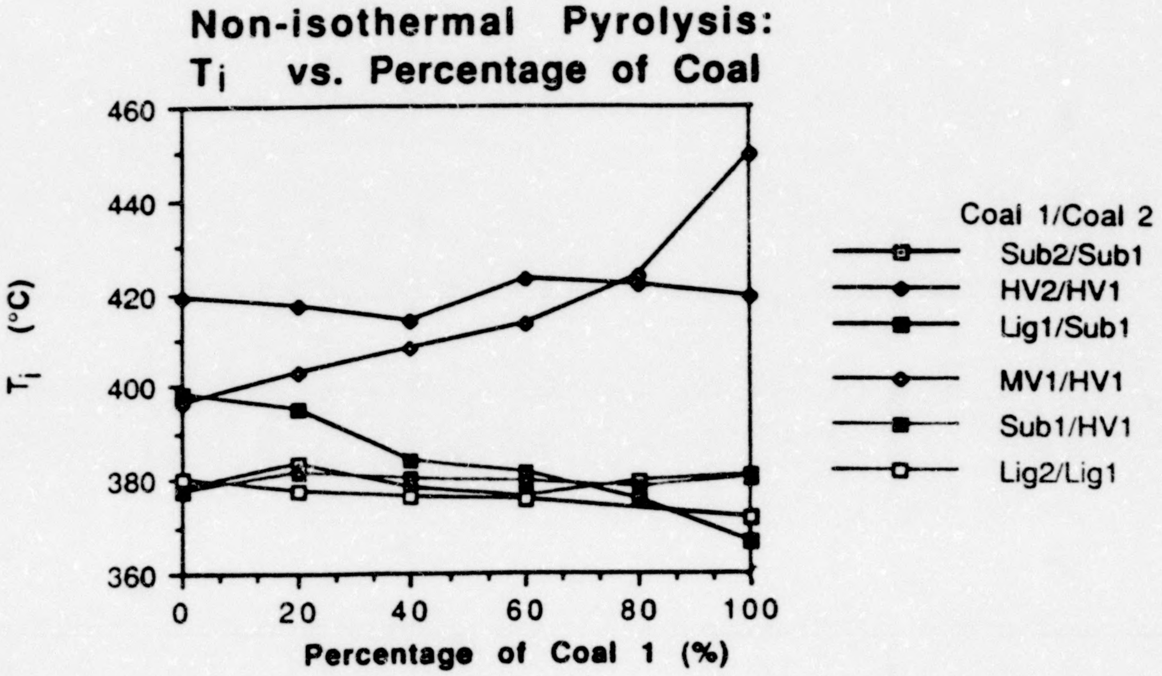

Figure 15. Non-isothermal Pyrolysis - T_i Values for Six Groups of Coal Blends.

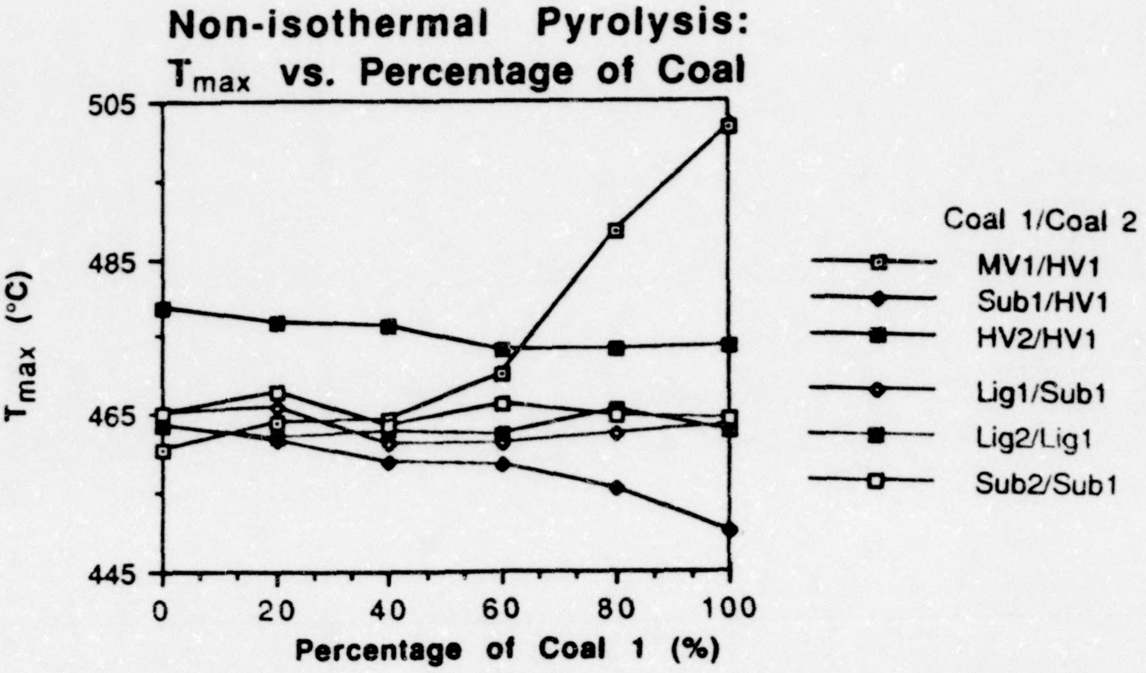

Figure 16. Non-isothermal Pyrolysis - T_{max} Values for Six Groups of Coal Blends.

°C when the MV1 content increased from 0% to 100%, and it did not exhibit an additive relationship. The experimental values found were lower than the calculated values. This is the same behavior noted for the T_i temperature for these coal blends. The experimental T_{max} and T_i values were both lower than the calculated values. However, there were no significant differences between the determined and calculated values for T_{max} for blends of HV1/HV2, Sub1/Lig1, HV1/Sub1, Sub1/Sub2 and Lig1/Lig2. For the Lig1/Lig2 blend, T_{max} remained almost constant within the temperature range of 462.2°C to 465.5°C. As discussed in the section on T_i, the five cases of blending mentioned above gave inconclusive evidence of an additive relationship. This once more indicates that T_i and T_{max} have the same kinetic meaning in the coal volatile release profile. They appear to be correlated and vary to the same relative degree.

c. $T_{1/2}$ - Temperature of 50% Weight Loss

The values for the kinetic parameter $T_{1/2}$ for coal blends HV2/HV1, Sub2/Sub1, and HV1/Sub1 appear to be nonadditive, as shown in Figure 17. For the HV1 and HV2 coal blend, when HV1 content increased from 0% to 100%, $T_{1/2}$ decreased from 514.4 °C to 493.9 °C. No linear trend was indicated by this curve. For the Sub1 and Sub2 coal blend, when Sub1 content increased from 0% to 100%, the $T_{1/2}$ values were randomly spread within the range of 526.7 °C to 513.7 °C (Figure 17). The values of $T_{1/2}$ for the other coal blends did not indicate a clear additive relationship. These nonadditive

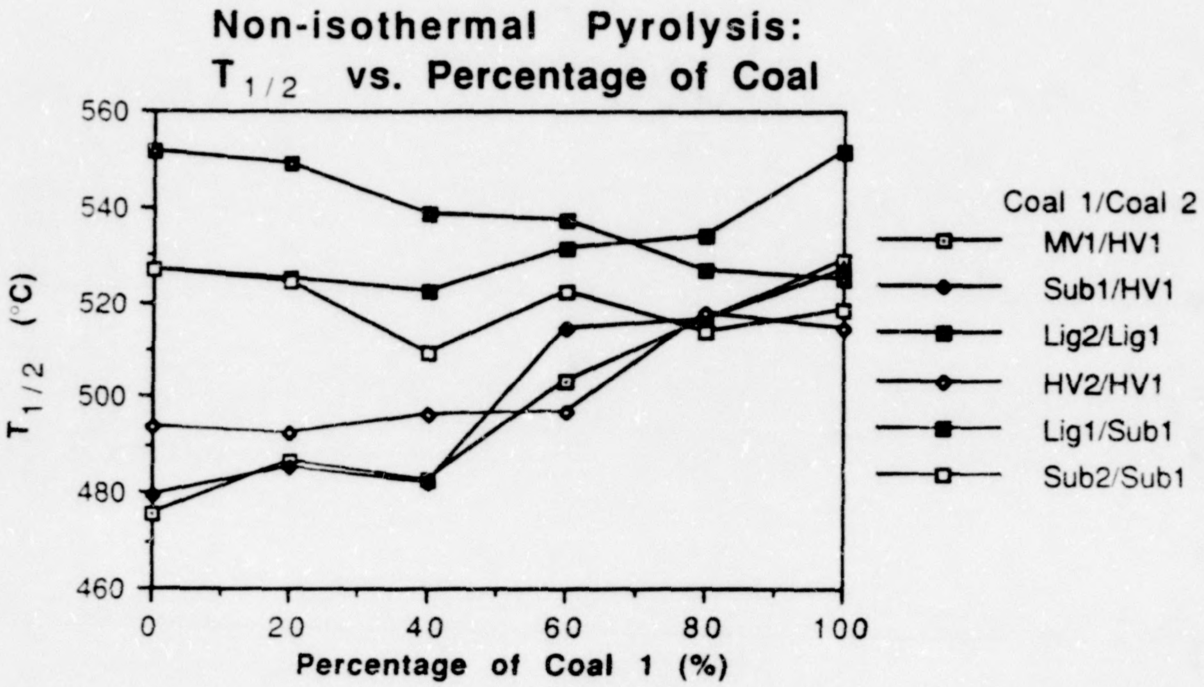

Figure 17. Non-isothermal Pyrolysis - $T_{1/2}$ Values for Six Groups of Coal Blends.

results may be due to the mixed catalysts effect. This effect may change the rate of pyrolysis decomposition and make decomposition reactions faster or slower for various blends. Therefore, T_{max}, T_i and $T_{1/2}$ may be influenced by this effect.

d. R_{max} - Reactivity at T_{max}

The values of R_{max} for coal blends MV1/HV1, HV2/HV1, Sub1/HV1 and Lig1/Sub1 appear to be nonadditive, as shown in Figure 18. For MV1 and HV1 coal blends, when MV1 content increased from 0% to 100%, Rmax decreased from 0.0595 min^{-1} to 0.0290 min^{-1}. Since the ranks of MV1 and HV1 are significantly different, most parameters for MV1/HV1 indicate a nonadditive relationship (Figures 15, 16, and 17). The R_{max} values for the other coal blends did not give conclusive evidence about an additive relationship. For Lig1 and Lig2 coal blends, when Lig2 content increased from 0% to 100%, Rmax increased from 0.0160 min^{-1} to 0.0194 min^{-1} (Figure 18). The R_{max} values for Lig1 and Lig2 were very close, and therefore the differences shown in their blends were insignificant. A nonadditive relationship could not be observed within such a narrow range. On the other hand, the mixed catalysts effect (synergism) may not be a factor if the ranks and ingredients of two coals are very similar.

Comparing the results of $T_{1/2}$ with R_{max}, in the case of Lig1/Sub1 coal blends, the experimental values were lower than the theoretical values for $T_{1/2}$, but higher than the theoretical values for R_{max}. In the case of HV2/HV1 coal blends, the experimental values were random with the first

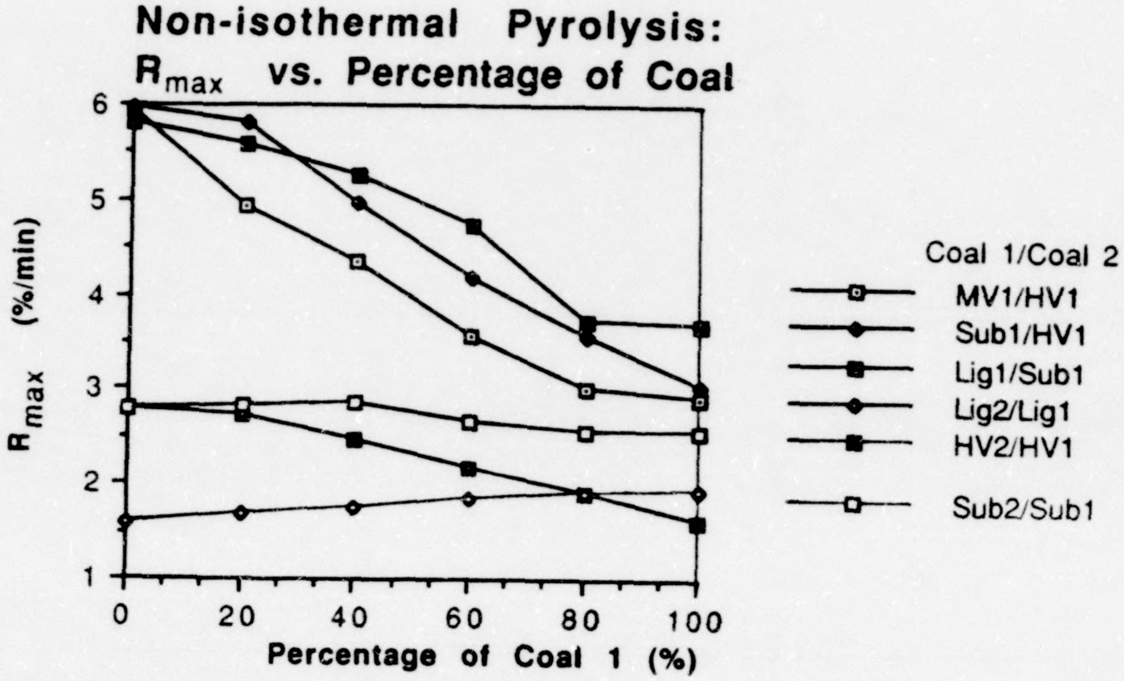

Figure 18. Non-isothermal Pyrolysis - R_{max} Values for Six Groups of Coal Blends.

three points lower than the calculated values and the last one higher for $T_{1/2}$. However, for R_{max} the experimental values were random with the first three points higher than the calculated values and the last one lower for R_{max}. These opposite effects again indicate that $T_{1/2}$ and R_{max} have an inversely proportional relationship. For example, when the reactivity (R_{max}) of the reaction becomes higher, the volatile matter will be released more quickly. Therefore, the temperature ($T_{1/2}$) at which half of the volatile matter has escaped should shift to a lower temperature.

e. Weight loss between 220 °C and 700 °C (W.L.)

The values of W.L. for coal blends MV1/HV1, and Lig1/Sub1 appear to be additive, as shown in Figure 19. The maximum relative error between experimental and calculated values was lower than ±4%. An additive trend was not obvious for the other groups of coal blends. In fact, synergism (mixed catalysts effect) can only change the speed of a decomposition reaction but not the amount of total weight loss during pyrolysis reaction due to the nature of catalysts.

In recent years, several researchers have been concerned with the catalyst effect in weight loss experiments. Tyler and Schafer (57), Franklin and co-workers (58), and Otake (59) studied the role of exchangeable cations in total weight loss and tar yield under a variety of reaction conditions. In general, they found that replacing the metal cations with hydrogen results in an increase in weight loss for pyrolysis. However, the value of volatile weight loss is not likely to

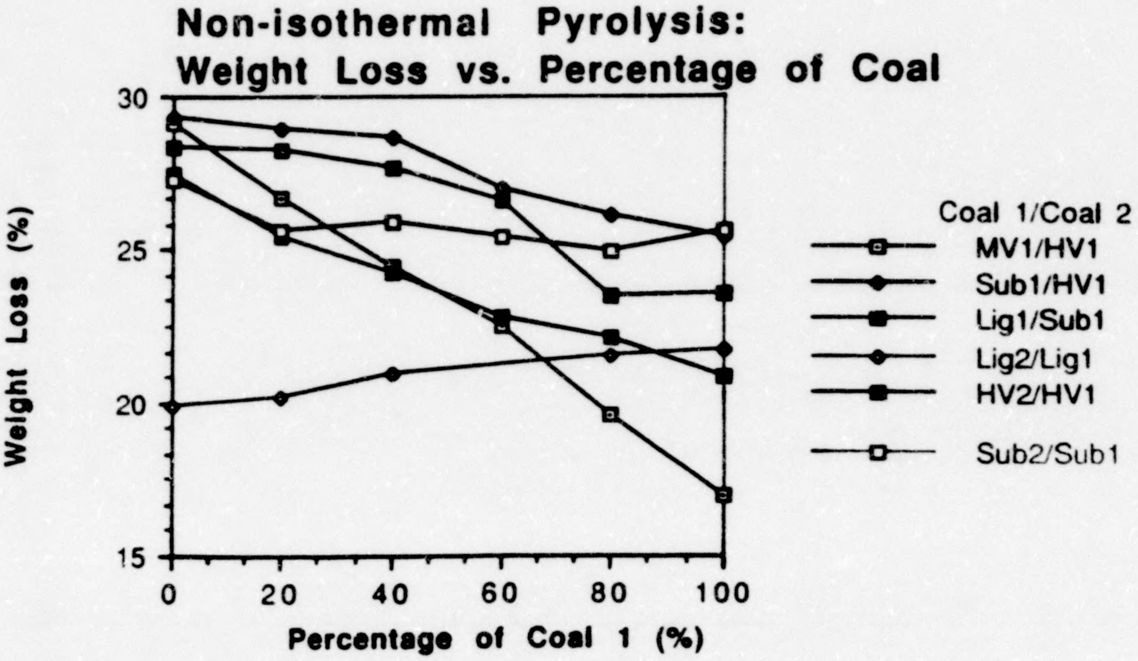

Figure 19. Non-isothermal Pyrolysis - Weight Loss Values for Six Groups of Coal Blends.

be influenced by the cations present in the various blends in this study.

From the results of experiments, the ranks of MV1 and HV1 exhibited the greatest difference; therefore, most of the parameters of MV1 and HV1 coal blends showed obvious additive or nonadditive trends. But the parameters of Sub1 and Sub2 were very close; therefore, most of the parameters of Sub1 and Sub2 were almost the same. Thus it is harder to find an additive or a nonadditive relationship.

5. Apparent Activation Energy in Pyrolysis

The Arrhenius coordinates used in constructing the log K versus 1/T plots from which the activation energies are derived were obtained from the experimental curves (e.g. Figure 1) by measuring the TG and DTG values at 8°C intervals throughout the devolatization range of 220°C to 600°C. Rates of weight loss can be read directly from the chart, and the weight of unreacted material at certain temperatures is determined by the difference between the weight at that temperature and the weight at the devolatization reaction end temperature (600°C). Values of K at each temperature level are calculated using Equation 1, and these are then plotted in the Arrhenius form, log K versus 1/T absolute (see Figure 20). From Equation 2, the gradient of this curve is numerically equal to the expression E/2.303R, and hence E can be calculated.

The Arrhenius plots for all of the MV1/HV1 coal blend

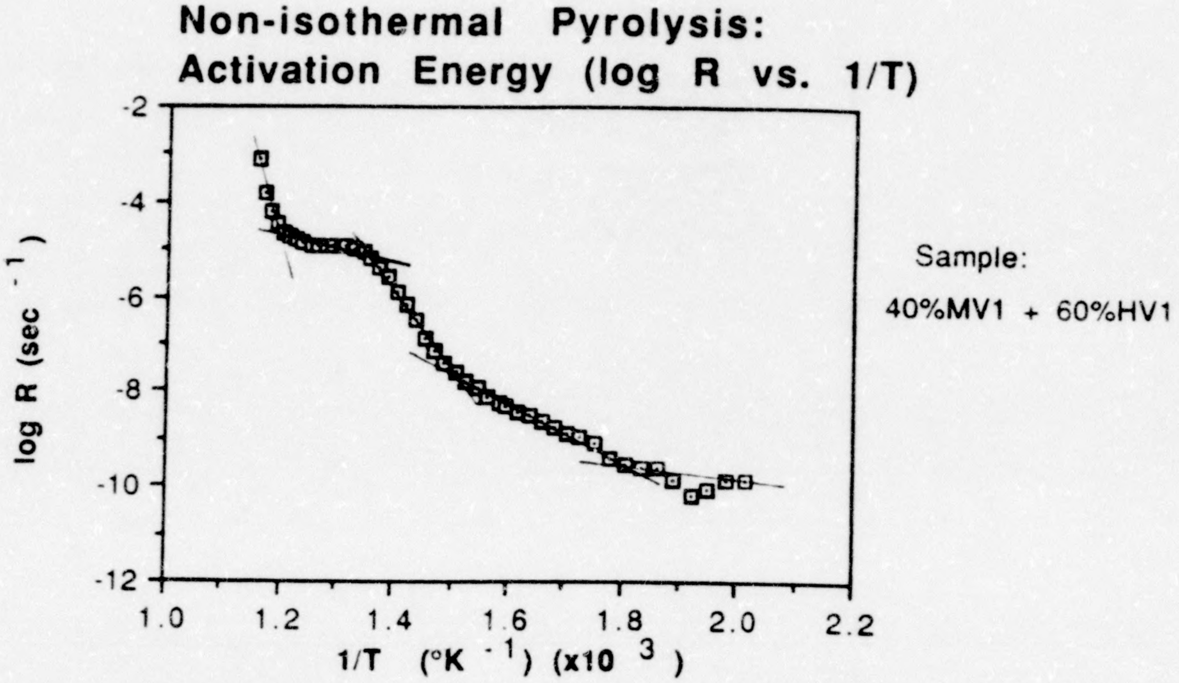

Figure 20. Non-isothermal Pyrolysis - Plots to Determine Activation Energy of Coal Blends. (40% MV1 + 60% HV1)

series display five regions of linearity. For coal blend 40%MV1+60%HV1 in Figure 20, the five regions are from 220 to 270°C (region 1), 270 to 390°C (region 2), 390 to 470°C (region 3), 470 to 560°C (region 4), and 560 to 600°C (region 5). From the gradients of these lines, the apparent activation energies associated with the five regions can be calculated as 13.10, 49.65, 137.5, 17.70, and 272.3 KJ/mol, respectively. The log A values for the five regions are -6.84×10^3, 1.29×10^3, 17.24×10^3, -2.18×10^3, and 34.52×10^3, and the ratios of E/log A are -1.92, 38.5, 7.97, -8.12 and 7.89 J/mol, respectively.

Although these values define the apparent activation energies associated with the various stages of pyrolysis, they denote nothing about the overall reactivity of the fuel. The reason they do not indicate overall reactivity is that they do not incorporate any term relating to the amount of sample reacted during each stage (40). To meet this requirement, the concept of a weighted mean apparent activation energy E_{ov}, as defined in Equation 4, has been adopted and in this particular case this is calculated as follows:

Weight loss over the first region of Arrhenius linearity (i.e., 220-270 °C) = 0.17%. and X_1 = 0.75%. Therefore,
$E_1X_1 = 13.10\times0.0075$ KJ/mol.

Weight loss over the second region of Arrhenius linearity (i.e., 270-390 °C) = 7.05%. and X_2 = 7.05%. Therefore,
$E_2X_2 = 49.65\times0.0705$ KJ/mol.

Applying the same treatment as above, we obtain:

$E_{ov} = 13.10\times0.0075 + 49.65\times0.0705 + 137.45\times0.4339 +$

$17.70 \times 0.4172 + 272.26 \times 0.0709 = 89.93$ (KJ/mol)

This treatment has been applied to a series of MV1/HV1 coal blends, and the resulting E_{ov} values are presented in Table 13. Also shown in Table 13 are the theoretical additive E_{ov} values for comparison.

The values of apparent activation energy were calculated using equation 3, which was defined in introduction section D. The MV1/HV1 coal blends which exhibited the greatest difference for most of the parameters gave a nonadditive activation energy. The average absolute error between experimental results and theoretical values was more than 5%. The experimental and theoretical values as well as the absolute errors are shown in Table 13. In the study of activation energy, only one peak between 220°C and 600°C should be useful (see Figure 1). This useful peak is due to the release of volatile matter. The activation energy is dependent mainly on the mechanism of the reaction. Catalysts can greatly influence the reaction mechanism as well as the value for the activation energy. The nonadditive results found for activation energy indicated that the presence of different types of mineral matter could have a profound mixed catalyst effect on pyrolysis kinetics and its mechanism.

A kinetic compensation effect was obvious for all the MV1/HV1 coal blends. We then compared all the log A values in regions 3 and 5 which were around 17×10^3 and 34×10^3. All the log A values in regions 1, 2, and 4 were insignificant because they were too small (less than 2.86×10^3). The E/log A values

TABLE 13

COMPARISON OF E_{ov} RESULTS FROM EXPERIMENTS AND CALCULATIONS

Coal Blends	Activation Energy (KJ/mol)		Relative Error(%)
MV1/HV1	Experimental	Theoretical	
0%/100%	87.17	87.17	
20%/80%	81.24	89.12	8.84
40%/60%	89.93	92.07	2.32
60%/40%	85.96	95.02	9.53
80%/20%	97.84	97.97	0.13
100%/0%	100.93	100.93	

in regions 3 and 5 for all coal blends were almost the same (E/log A around 8.0). It may indicate that the reactions within regions 3 and 5 have the same mechanisms. It is proposed that the compensation effect could be involved in the reaction mechanisms of these coal blends. Up to this time there has been no major study of how the compensation effect can be related to the reaction mechanism. For the 40%MV1/60% HV1 coal blend in Figure 20, E_3/log A_3 for region 3 was 7.97 and E_5/log A_5 for region 5 was 7.89. With such close E/log A values, the same kinetic mechanism could possibly be occurring in regions 3 and 5.

B. Combustion Behavior of Coal Blends

We next wanted to consider the combustion behavior of coal blends. This was done using both isothermal and non-isothermal conditions. Once again the different kinetic parameters were considered to see whether or not an additive or nonadditive relationship was apparent.

1. TG curve

In the combustion process, all the samples were exposed to an atmosphere of air. Typical TG curves for two coal blend samples in air are shown in Figures 21 and 22. Figure 21 shows the non-isothermal heating process for combustion and Figure 22 shows the isothermal combustion process. The major combustion decomposition stages can be observed for all the coal blend samples which are represented

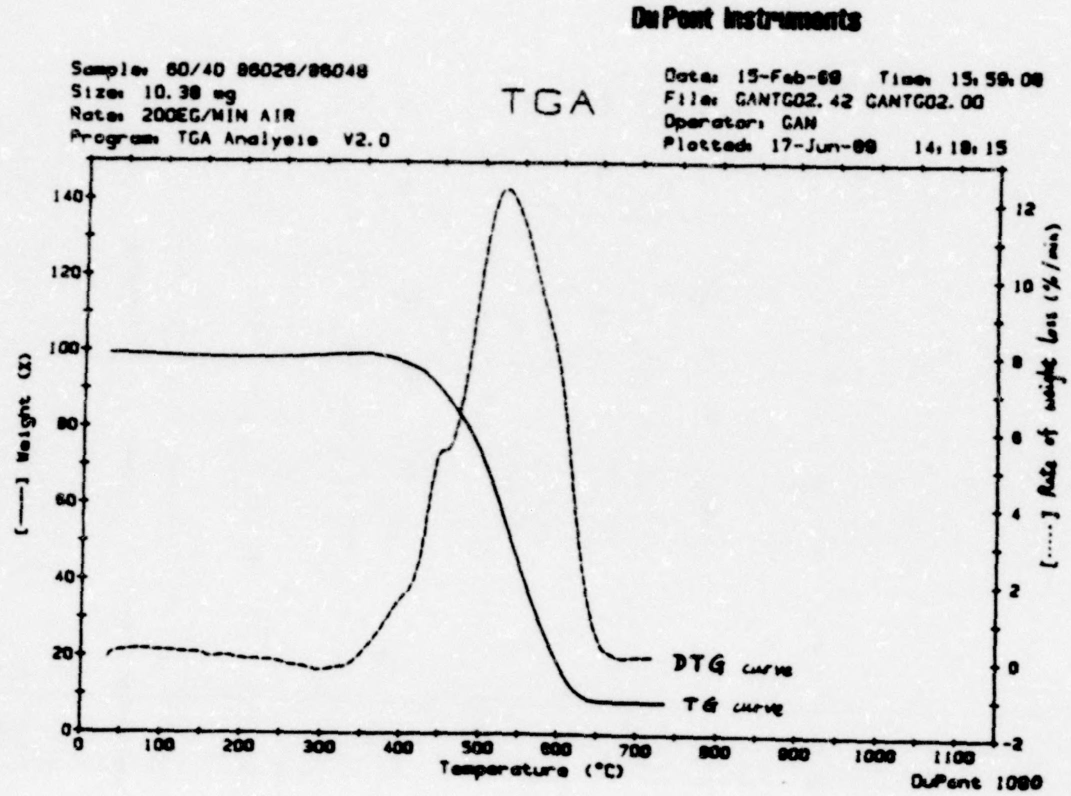

Figure 21. TG Heating Curve - 60% MV1 + 40% HV1 Coal Blend in Air under Non-isothermal Conditions.

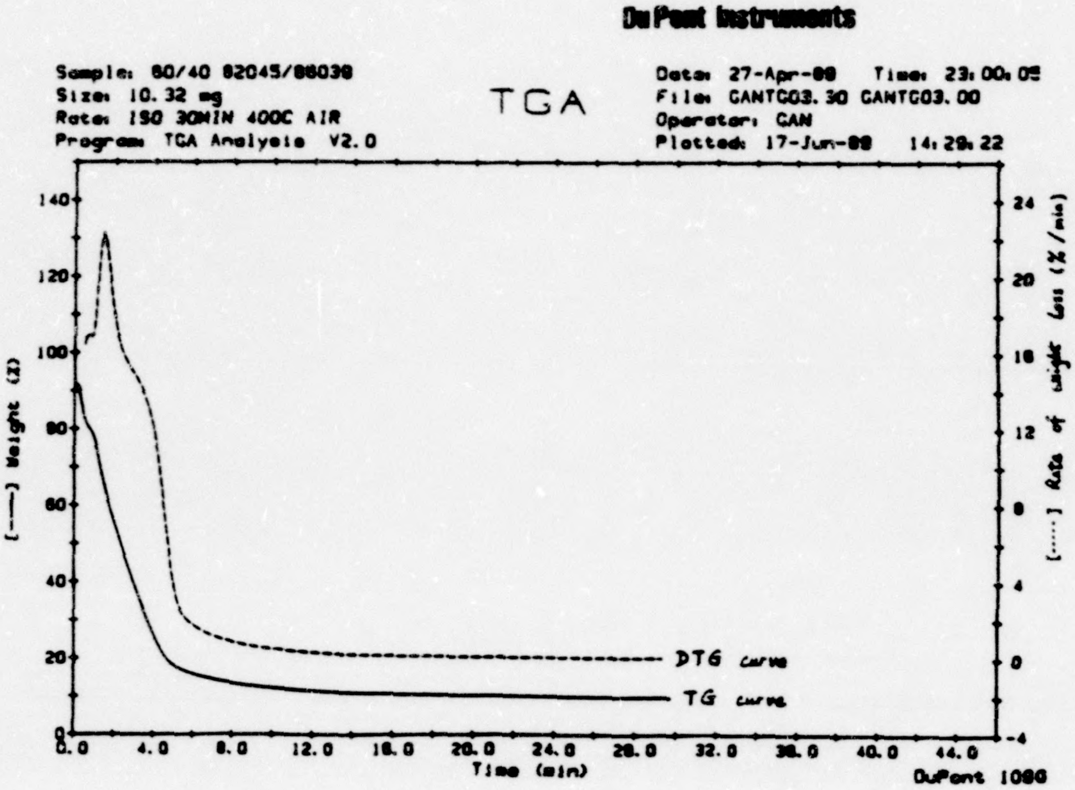

Figure 22. TG Heating Curve - 60% Sub2 + 40% Sub1 Coal Blend in Air under Isothermal Conditions.

by the major peak on the DTG curve.

In the experiments, we used six series of coal blends and each series contained 0%, 20%, 40%, 60%, 80%, 100% component contents to test general rules of coal blend properties during a non-isothermal process and an isothermal process. The results obtained are given in the following sections.

2. Non-isothermal conditions

Non-isothermal combustion involves a chemical change when a coal blend sample is heated in a non-isothermal furnace in the presence of air. Figure 21 shows the TG curve for a coal blend during a non-isothermal combustion process. The values of five important kinetic parameters were studied using these types of TG curves. The results for additivity or nonadditivity of the five thermal parameters for coal blends are given in Table 14.

a. T_i - Initial Reaction Temperature

The values of T_i for coal blends HV1/Sub1 appeared to be nonadditive, because some of the T_i data was out of the allowed error range of ±3% for an additive relationship, as shown in Figure 23. The nonadditive relationship was clear because the T_i values for HV1 and Sub1 are very different. The values of T_i for the other coal blends HV2/HV1. MV1/HV1, Sub1/Lig1, Sub1/Sub2 and Lig2/Lig1 did not show this relationship very clearly. For Lig1 and Lig2 coal blends, when the Lig2 content increased from 0% to 100%, T_i remained almost constant within the temperature range of 293.0

TABLE 14

RELATIONSHIP OF PARAMETER VALUES FOR EACH SET OF COAL BLENDS UNDER NON-ISOTHERMAL COMBUSTION CONDITIONS

	Relationship Appears		
Parameters	Additive	Nonadditive	Inconclusive
T_i		Sub1/HV1	HV2/HV1, Sub2/Sub1 MV1/HV1,Lig2/Lig1 Lig1/Sub1
T_{max}		Sub1/HV1	HV2/HV1, Sub2/Sub1 MV1/HV1,Lig2/Lig1 Lig1/Sub1
R_{max}		Sub2/Sub1 MV1/HV1 Sub1/HV1 Lig2/Lig1	HV2/HV1, Lig1/Sub1
Weight loss	Sub2/Sub1 MV1/HV1 Lig2/Lig1 Lig1/Sub1		HV2/HV1, Sub1/HV1
Residue	MV1/HV1 Lig1/Sub1		HV2/HV1, Sub2/Sub1 Sub1/HV1, Lig2/Lig1

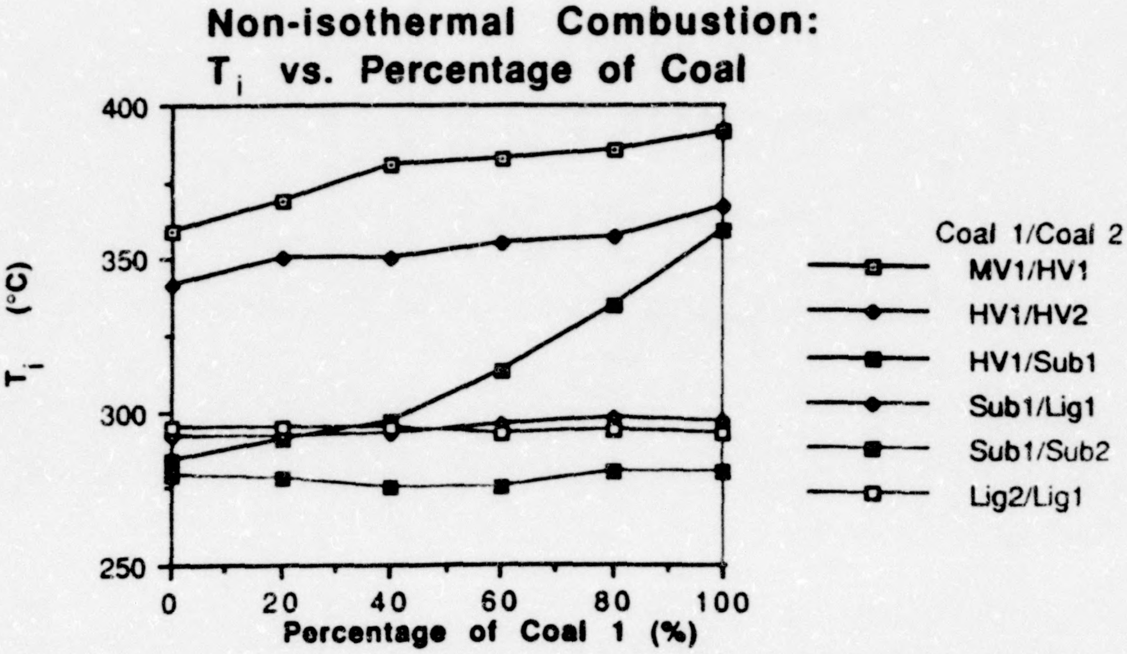

Figure 23. Non-isothermal Combustion - T_i Values for Six Groups of Coal Blends.

$^{\circ}C$ and 295.2 $^{\circ}C$ (Figure 23). It was hard to show any nonadditive relationship within such a small temperature range. Different coals include different mineral matter components such as K, Ca, Na or Co salts which might exhibit different catalytic effects in the combustion process. A series of coal blends with different proportions of two types of mineral matter may display a nonadditive catalytic effect.

b. T_{max} - Temperature of Maximum Rate of Weight Loss

The values of T_{max} for coal blends HV1/Sub1, appeared to be nonadditive because some the T_{max} values were not located within the allowed error range for an additive relationship, as shown in Figure 24. But the values of T_{max} for the other coal blends like Sub1/Sub2 and Lig2/Lig1 seem to be constant. For Sub1 and Sub2 coal blends, when the Sub1 content increased from 0% to 100%, T_{max} remained almost constant within the temperature range of 386.0 $^{\circ}C$ and 389.5 $^{\circ}C$. It was a general observation that for two largely different ranks of coals, when the parameters of the two individual coals showed significant differences, the parameters of their blend showed an obvious nonadditive trend. However, for two ranks of coal that were not significantly different, the parameters of the individual coals were very close, and the parameters of their blend remained almost constant.

c. R_{max} - Reactivity at T_{max}

The values of R_{max} for coal blends HV1/Sub1, MV1/HV1, Lig2/Lig1 and Sub1/Sub2 appeared to be nonadditive,

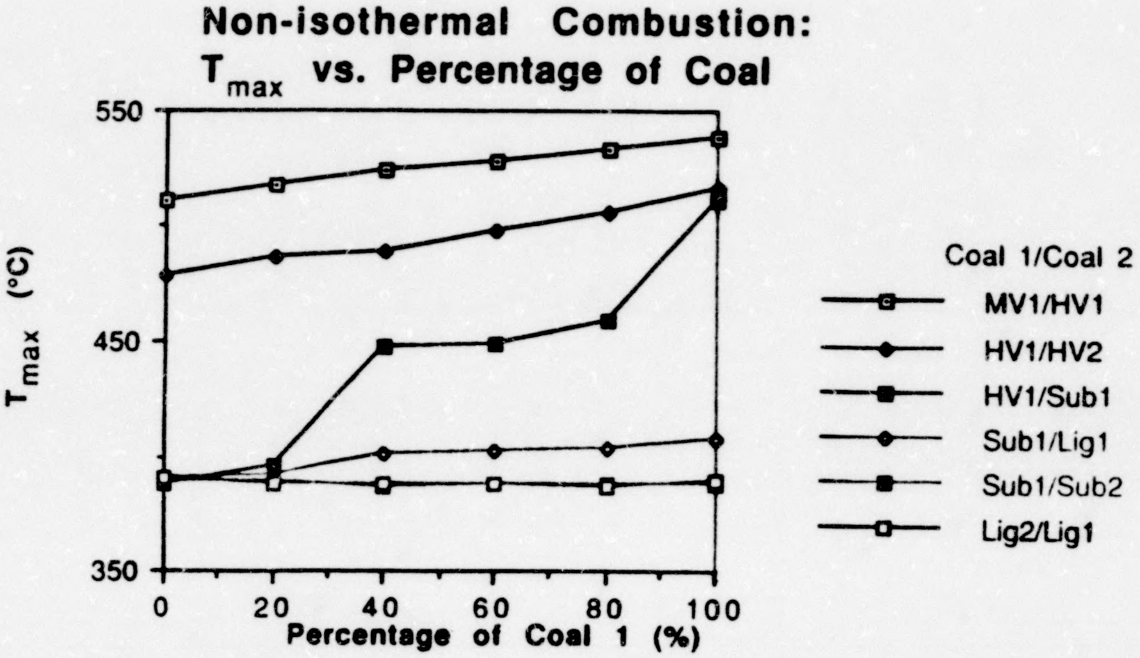

Figure 24. Non-isothermal Combustion - T_{max} Values for Six Groups of Coal Blends.

as shown in Figure 25. The maximum relative error for the R_{max} values of these coal blends when compared to the calculated values were larger than the allowed error range ±4%. Thus, a nonadditive relationship was deduced. The values of R_{max} for coal blends Lig1/Sub1 and HV1/HV2 showed almost a constant relationship (Figure 25). One can see from the groupings in Figure 25 that the lines obtained do not display characteristics of additive samples. Some differences were quite large, especially in blends involving low rank coals. For example, HV1/Sub1 blends showed the most clear nonadditive relationship (Figures 23-25).

d. Dry basis weight-loss between 220 °C and 750 °C (W.L.)

Dry basis Weight-loss (W.L.,%) between 220°C and 750°C is determined by the equation:

$$W.L.(\text{dry basis}) = W.L. \times 100/(100 - \text{Moisture\%})$$

Here, Moisture% is the percentage weight loss between the initial (30 °C) temperature and 220 °C. The values of W.L.(dry basis) for coal blends MV1/HV1, Sub1/Sub2, Sub1/Lig1 and Lig2/Lig1 appeared to be additive. This meant that all W.L. values for these coal blends were within the allowed error range, as shown in Figure 26. For example, for MV1 and HV1 coal blends, when MV1 content increased from 0% to 100%, W.L.(dry basis) increased from 88.74% to 95.84%. However, for HV1 and Sub1 coal blends, when HV1 content increased from 0% to 100%, the W.L.(dry basis) remained almost constant within the percentage range of 88.56% to 90.64%. This is because the

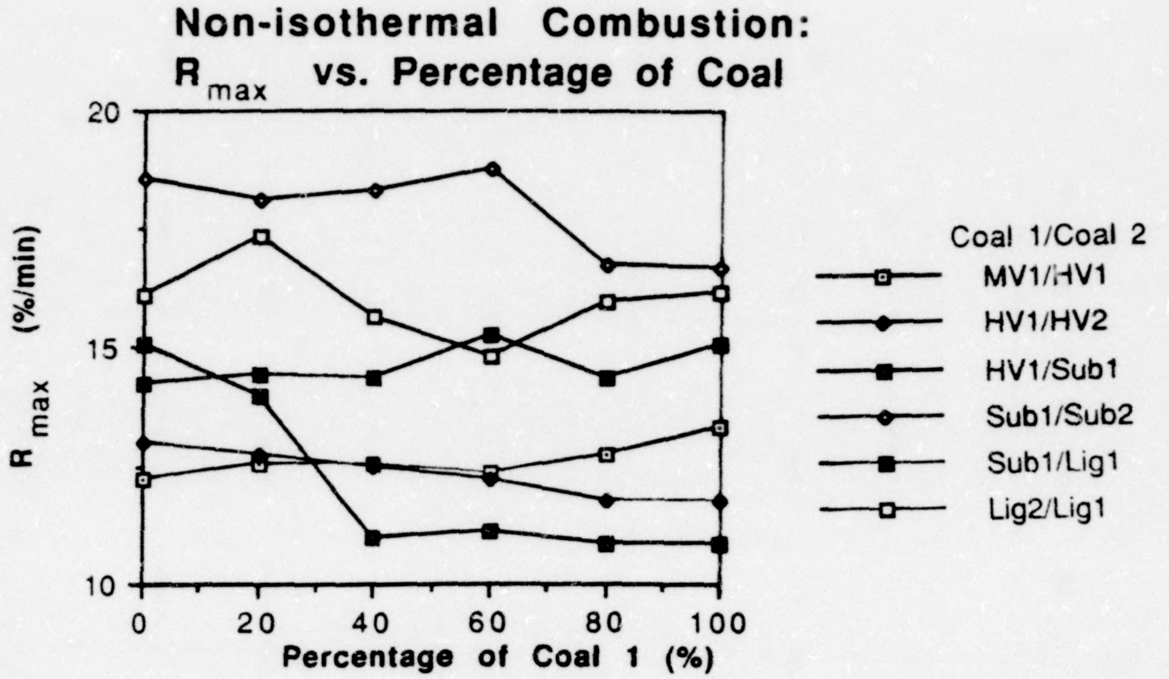

Figure 25. Non-isothermal Combustion - R_{max} Values for Six Groups of Coal Blends.

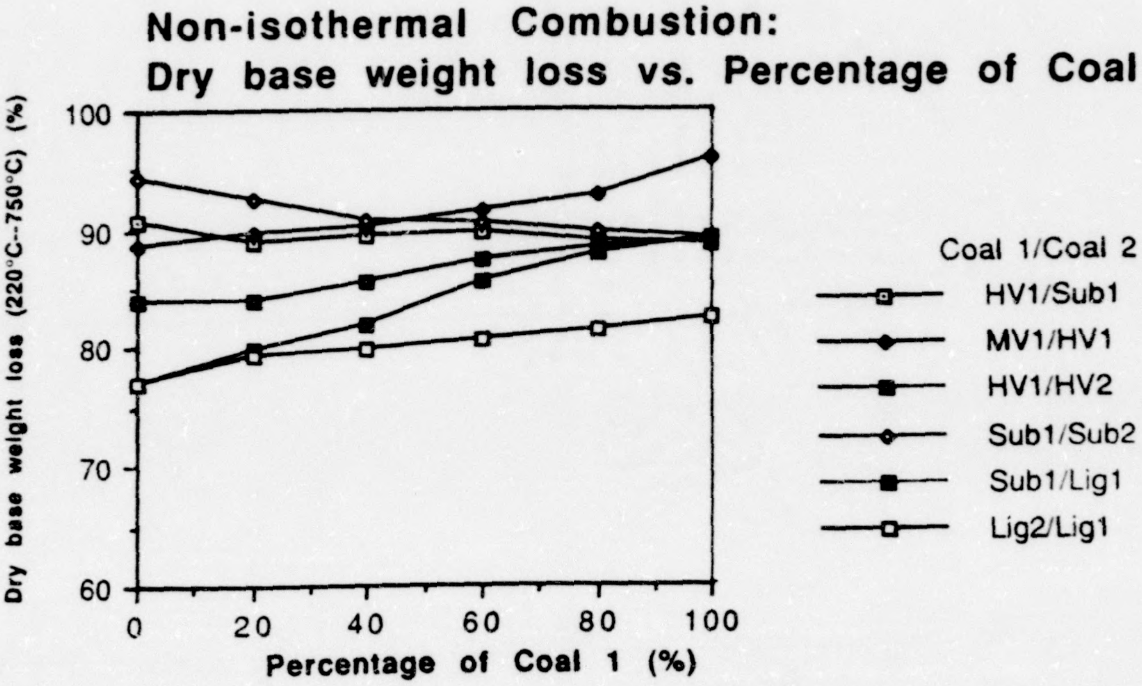

Figure 26. Non-isothermal Combustion - Dry Base Weight Loss Values for Six Groups of Coal Blends.

W.L.(dry basis) values of HV1 and Sub1 are very close. The W.L.(dry basis) and residue values do not appear to have an additive nature. As we know, catalytic effects can only influence the speed of combustion. That is why they can influence T_i, T_{max} and R_{max}, but catalysts effects cannot influence the total weight-loss.

e. Residue

Residue (%) is the percentage of the material which remains after the sample has been combusted completely. The values of residue for MV1/HV1, Lig1/Sub1 coal blends appeared to be additive, as shown in Figure 27. Considering the allowed error conditions, the experimental values of residue were close to the calculated values pointing to an additive trend. For MV1 and HV1 coal blends, when MV1 content increased from 0% to 100%, residue decreased from 11.26% to 6.36%. The residue values of these individual coal samples are significantly different, therefore the residue values of their blends also show significant differences.

f. Weight-gain

The TG curves of some higher rank coal blend samples like MV1/HV1 and HV1/HV2 show a small weight-gain peak (240 $^{\circ}$C--340 $^{\circ}$C) prior to the major weight-loss decomposition. This is due to the absorption of oxygen by the coal blend when the sample is heated. Unlike the coal pyrolysis or combustion reaction, the process of absorption of oxygen is not a reaction catalyzed by mineral matter. Also at this time the temperature is not high enough for the catalysts to be active.

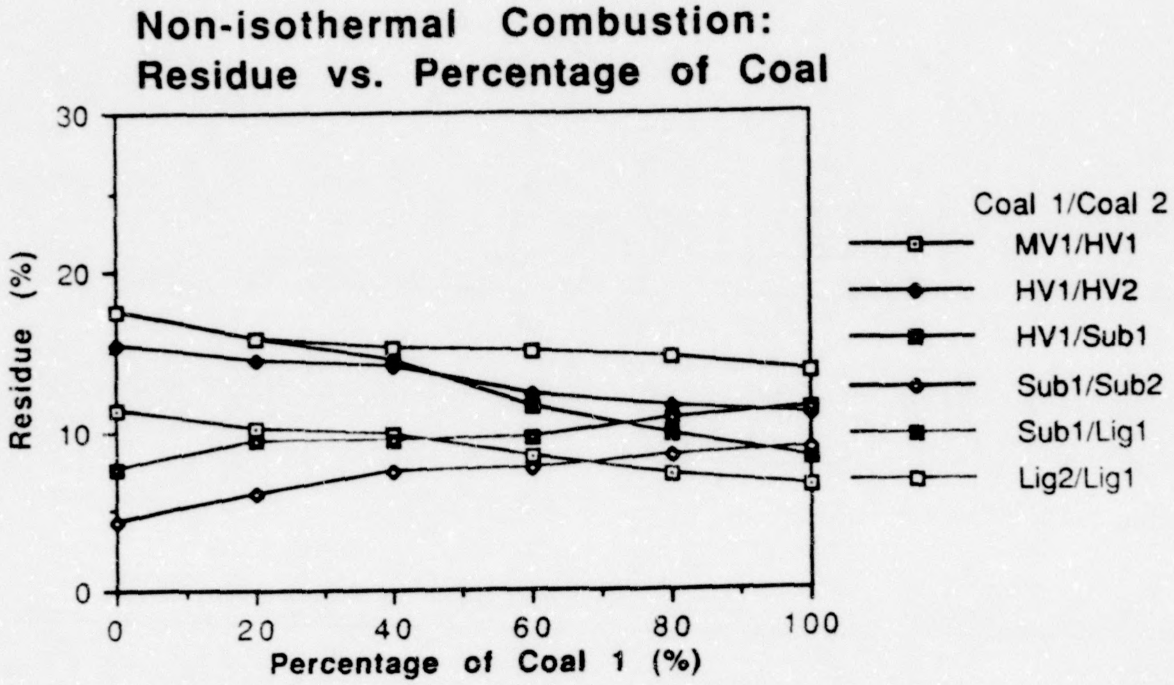

Figure 27. Non-isothermal Combustion - Residue Values for Six Groups of Coal Blends.

For the TG curves, several parameters (T_{max}, R_{max}, maximum weight) relating to the small weight-gain peak seem to have an additive relationship. The results of MV1/HV1 and HV1/HV2 coal blends obtained are shown in Figures 28-30. All the experimental values are close to the calculated additive values. Here, maximum weight is the weight value when the weight starts to decrease and R (rate of weight loss) starts to become positive. In the beginning, weight loss or weight gain is very insignificant. Therefore we can use the weight at 215 °C as the original weight (100%) for all the samples.

g. Secondary peak

The TG curves of some lower rank coal blend samples show a small secondary peak (490 °C--540 °C) following the major weight-loss decomposition. This is due to the slower combusting materials, some of which decompose later. For the parameters of the secondary peak, we found an additive trend for the coal blends. From the TG curves, the secondary peak is a weak peak and occurs at high temperatures. For Lig1 and Lig2 coal blends, when Lig2 content increased from 0% to 100%, the secondary peak T_{max} decreased from 542.0 °C to 487.8 °C, and the secondary peak R_{max} increased from 1.11%/min to 2.80%/min, as shown in Figures 31 and 32. The experimental errors are within the allowed error range.

3. Isothermal conditions

Isothermal combustion involves a chemical change when a sample is heated at a fixed temperature in the presence

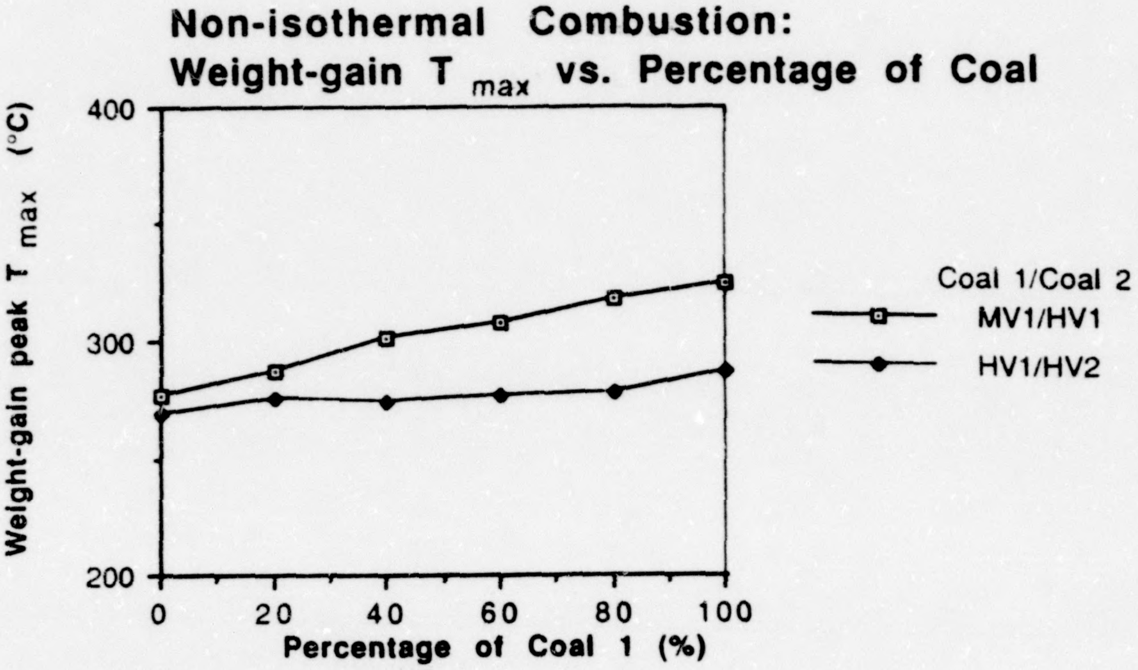

Figure 28. Non-isothermal Combustion - Weight Gain T_{max} Values for Two Groups of Coal Blends.

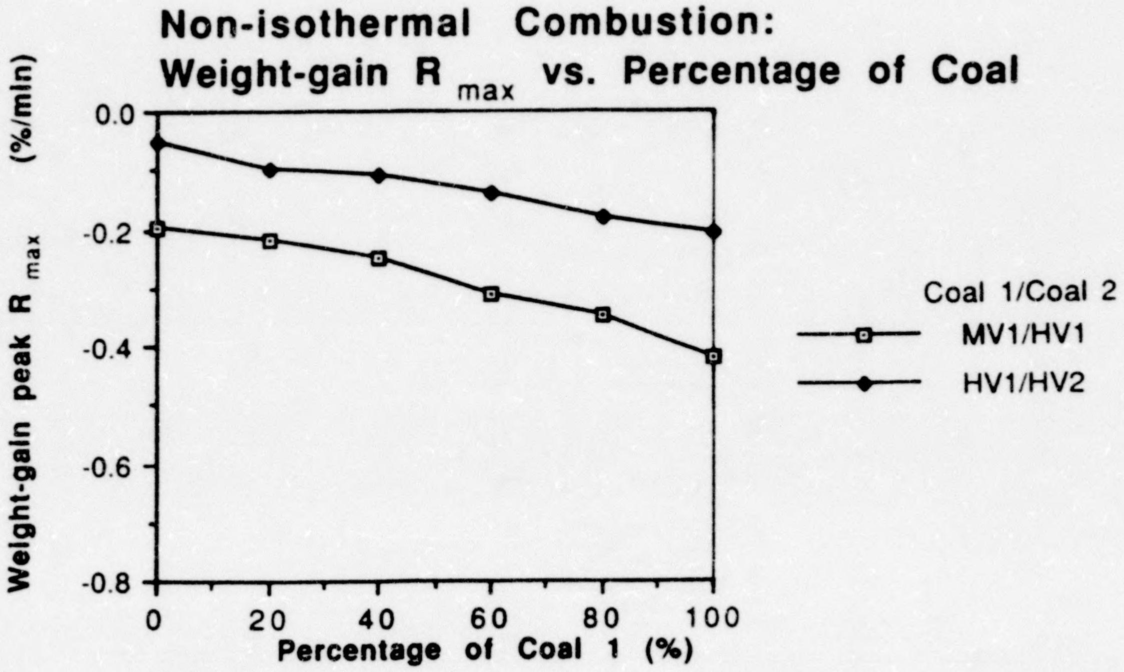

Figure 29. Non-isothermal Combustion - Weight Gain R_{max} Values for Two Groups of Coal Blends.

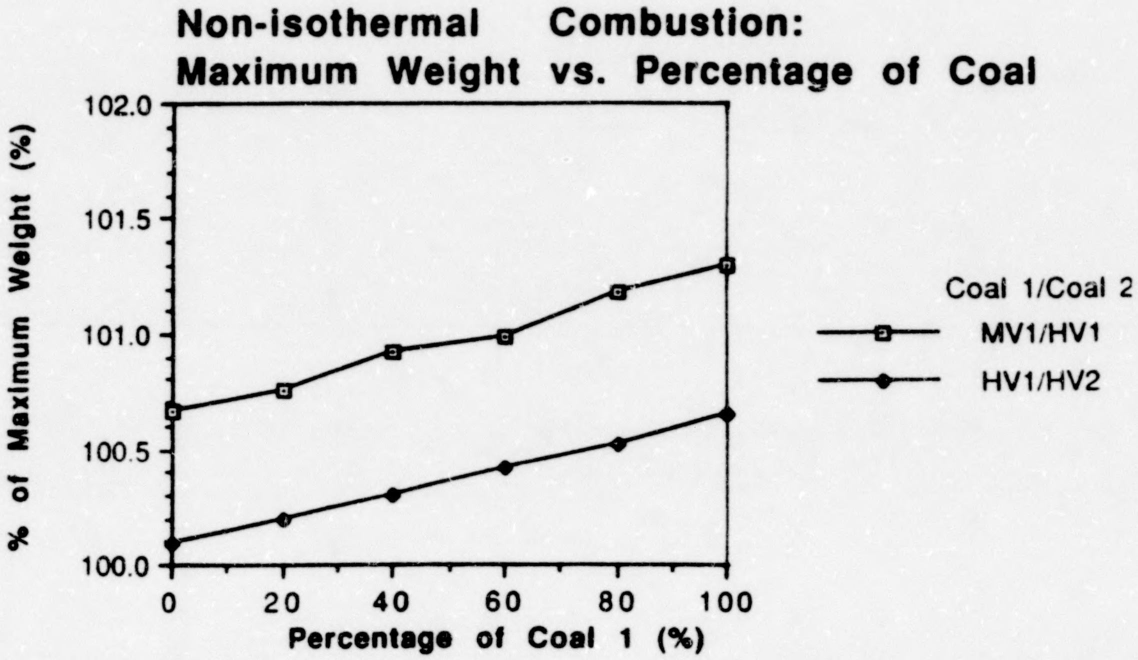

Figure 30. Non-isothermal Combustion - Maximum Weight Values for Two Groups of Coal Blends.

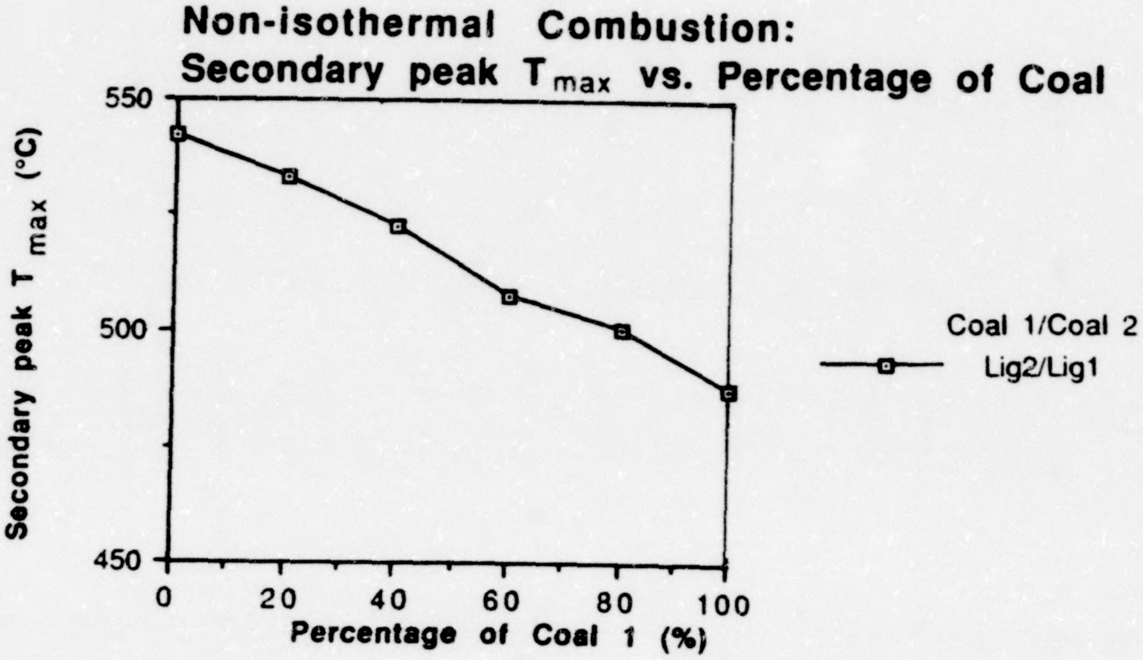

Figure 31. Non-isothermal Combustion - Secondary Peak T_{max} Values for Lig2/Lig1 Coal Blends.

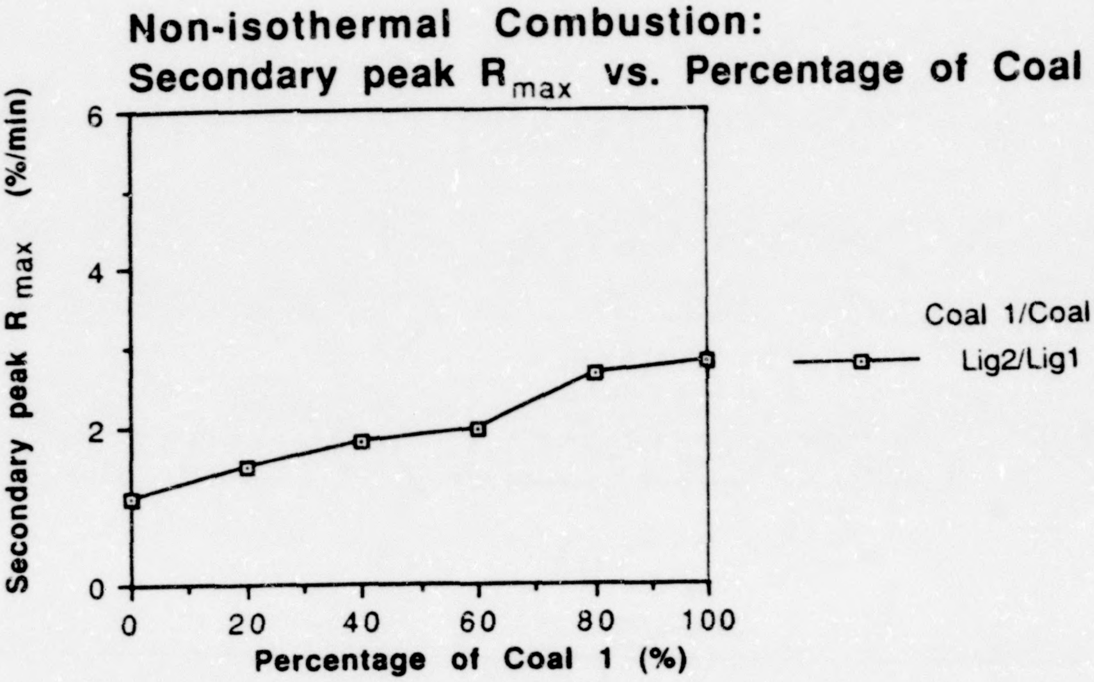

Figure 32. Non-isothermal Combustion - Secondary Peak R_{max} Values for Lig2/Lig1 Coal Blends.

of air. Figure 22 shows the TG heating curve for a coal blend during the isothermal combustion process. Five important kinetic parameters were studied using these conditions and the results of additivity or nonadditivity of these parameters for coal blends are showed in Table 15.

a. t_{max} - Time of Maximum Rate of Weight Loss

The time, t_{max} (min), is the time at which the maximum rate of weight-loss occurred. The values of t_{max} for coal blends MV1/HV1 and HV1/Sub1 show an additive relationship. All the data were found within the allowed error range for calculated values, as shown in Figure 33. For MV1 and HV1 coal blends, when MV1 content increased from 0% to 100%, t_{max} increased slightly from 0.80 min to 1.07 min. Because the t_{max} values for the individual coals are very close, the t_{max} for most coal blends such as HV1/HV2, Sub1/Sub2, Sub1/Lig1 and Lig2/Lig1 appeared to be almost constant. For Sub1 and Lig1 coal blends, when Sub1 content increased from 0% to 100%, t_{max} remained almost constant within the time range of 1.33 min to 1.47 min.

b. R_{max} - Reactivity at t_{max}

R_{max} (%/min) is the reactivity at t_{max}, the value for the maximum rate of weight-loss. The values of R_{max} for coal blends MV1/HV1, Lig2/Lig1, and HV1/Sub1 appear to be additive. The maximum relative error agreed with the allowed relative error for an additive trend, as shown in Figure 34. For MV1 and HV1 coal blends, when MV1 content increased from 0% to 100%, R_{max} decreased from 32.05%/min to 17.57%/min. The

TABLE 15

RELAIONSHIP OF PARAMETER VALUES FOR EACH SET OF COAL BLENDS UNDER ISOTHERMAL COMBUSTION CODITIONS

	Relationship Appears		
Parameters	Additive	Nonadditive	Inconclusive
t_{max}	MV1/HV1 HV1/Sub1		Lig2/Lig1, HV1/HV2 Sub2/Sub1, Lig1/Sub1
R_{max}	MV1/HV1 Lig2/Lig1 HV1/Sub1		HV1/HV2, Sub2/Sub1 Lig1/Sub1
$t_{break\ point}$		HV1/Sub1 HV1/HV2 Sub2/Sub1	Lig2/Lig1, MV1/HV1 Lig1/Sub1
$t_{combustion\ end\ point}$		MV1/HV1 HV1/Sub1 HV1/HV2 Sub2/Sub1	Lig1/Sub1 Lig2/Lig1
Residue		MV1/HV1 HV1/Sub1 HV1/HV2 Sub2/Sub1	Lig2/Lig1 Lig1/Sub1

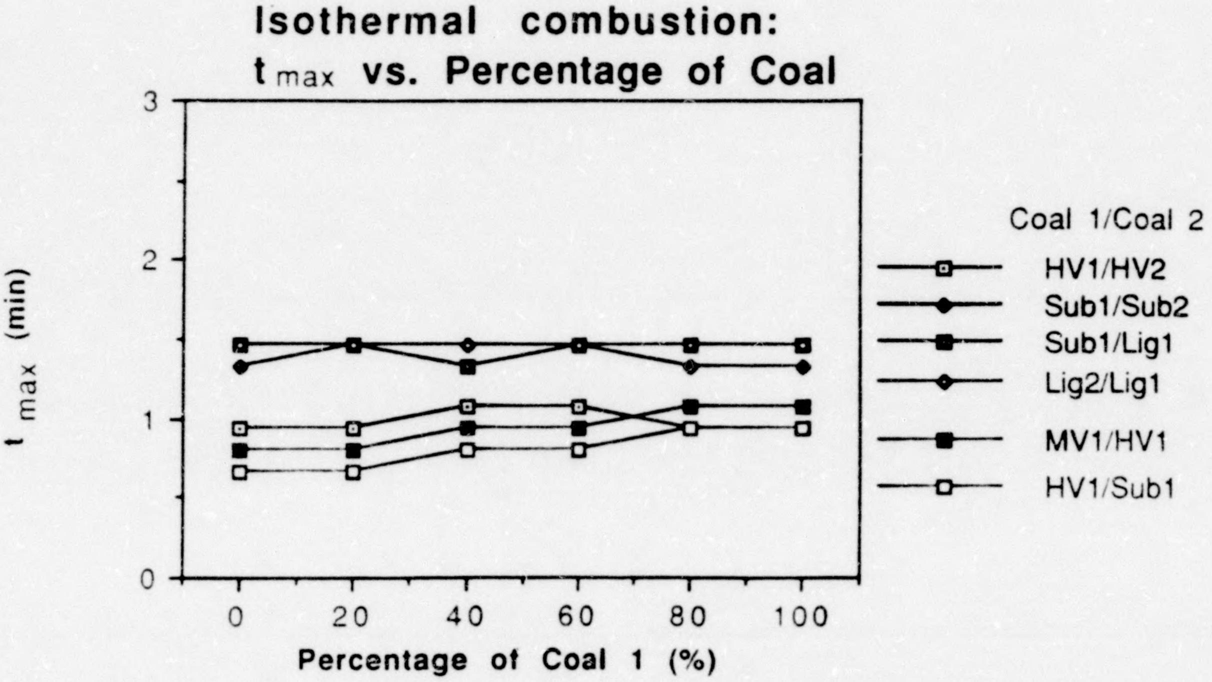

Figure 33. Isothermal Combustion - t_{max} Values for Six Groups of Coal Blends.

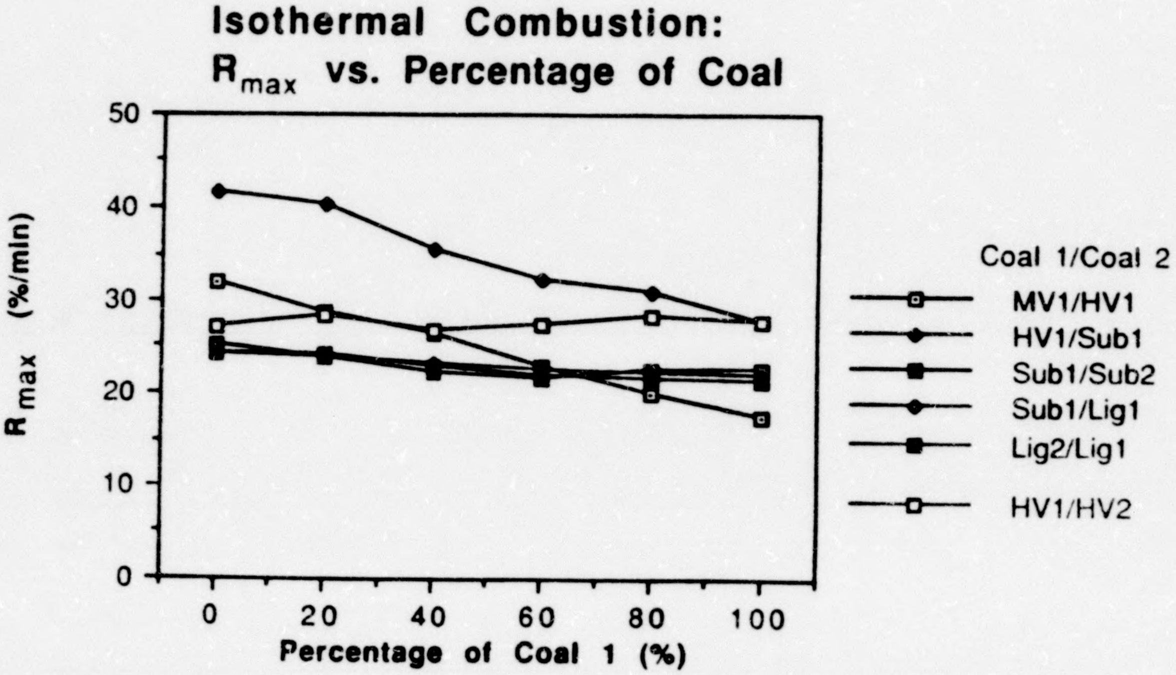

Figure 34. Isothermal Combustion - R_{max} Values for Six Groups of Coal Blends.

values of R_{max} for the other coal blends appear to be constant. For HV1 and HV2 coal blends, when HV1 content increased from 0% to 100%, R_{max} remained almost constant within the R_{max} range of 26.93%/min and 28.53%/min. For isothermal combustion, the temperature effect played a more important role than the catalysts' effect within the first two minutes. Although the temperature of the furnace remained a constant value from the beginning to the end, the temperature of the sample which had just been introduced to the furnace does not reach the chosen temperature within the first two minutes. The values of t_{max} and R_{max} are obtained at the very beginning of the heating curve around the first minute. At this time, the catalyst is not active yet; thus, the catalysts' effect may not be significant.

c. $\underline{t}_{break\ point}$

The time, $t_{break\ point}$ (min), is the time at which the maximum change in rate of weight-loss occurred. Among a series of differences for R (rate of weight loss) between two neighboring points, the maximum change of two differences occurred at the break point. The values of $T_{break\ point}$ for most coal blends HV1/HV2, HV1/Sub1, and Sub1/Sub2 appear to be nonadditive, as shown in Figure 35. The experimental values were out of the allowed error range for an additive relationship. This may be due to the mixed catalyst effect. Because the ranks of Lig1 and Lig2 are very close, the $t_{break\ point}$ values of Lig1, Lig2, and their blends did not show any significant differences.

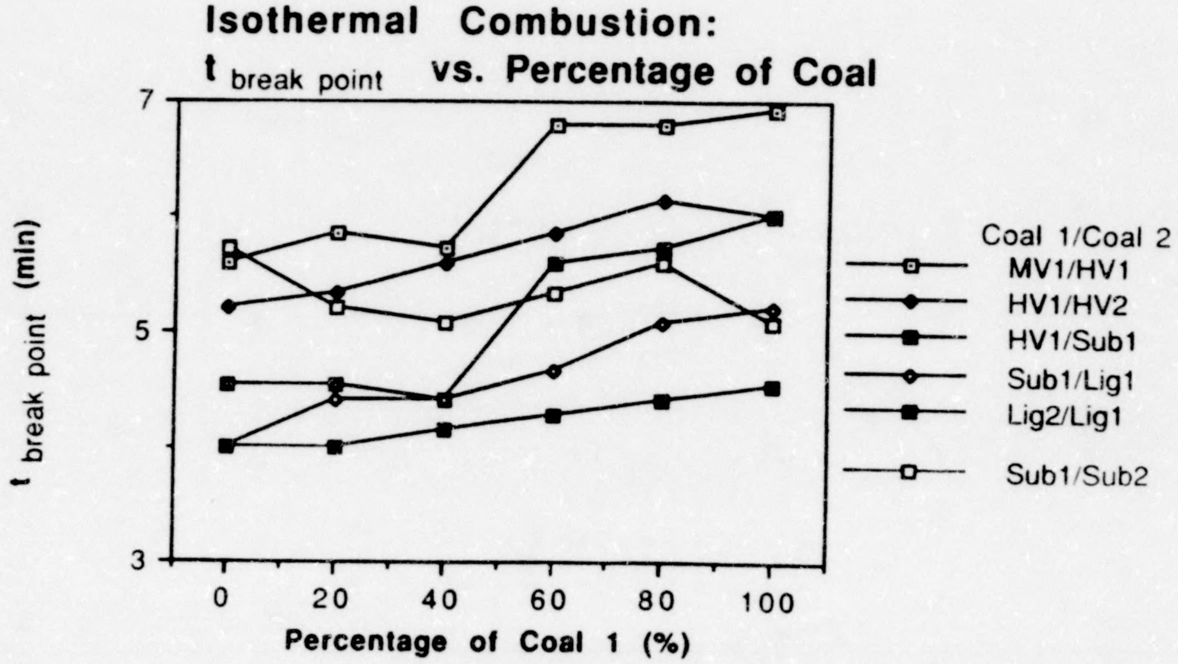

Figure 35. Isothermal Combustion - $t_{\text{break point}}$ Values for Six Groups of Coal Blends.

d. $\underline{t}_{\text{combustion end point}}$

The time, $t_{\text{combustion end point}}$ (min), is the time at which the rate of weight-loss decreased to 0.10%/min. At this time, the weight-loss usually remained at zero. Therefore, the time value is regarded as $t_{\text{combustion end point}}$ when the rate of weight-loss reaches 0.10%/min. The values of $t_{\text{combustion end point}}$ for most coal blends appear to be nonadditive, especially for the HV1/Sub1 coal blend, as shown in Figure 36. Most experimental values were not found in the allowed error range for an additive relationship. This may also be due to the mixed catalyst effect which changes the reaction speed and the time for combustion to end.

e. Residue

The values of residue for HV1/HV2, MV1/HV1, HV1/Sub1, and Sub1/Sub2 coal blends showed a nonadditive relationship when determined by calculation. The results indicated that the maximum relative error between experimental values and theoretical values for an additive trend were higher than the allowed relative error, as shown in Figure 37. Due to isothermal conditions, the system's temperature was never higher than the assigned temperature (400°C-600°C). Figure 21 (non-isothermal combustion conditions) shows that at temperatures exceeding 400°C or 600°C (desired isothermal temperatures) some combustible volatile matter would still decompose. Therefore, the residue values for isothermal conditions were not the same as the ash content value. The residue value may also be effected by a catalyst and thus may

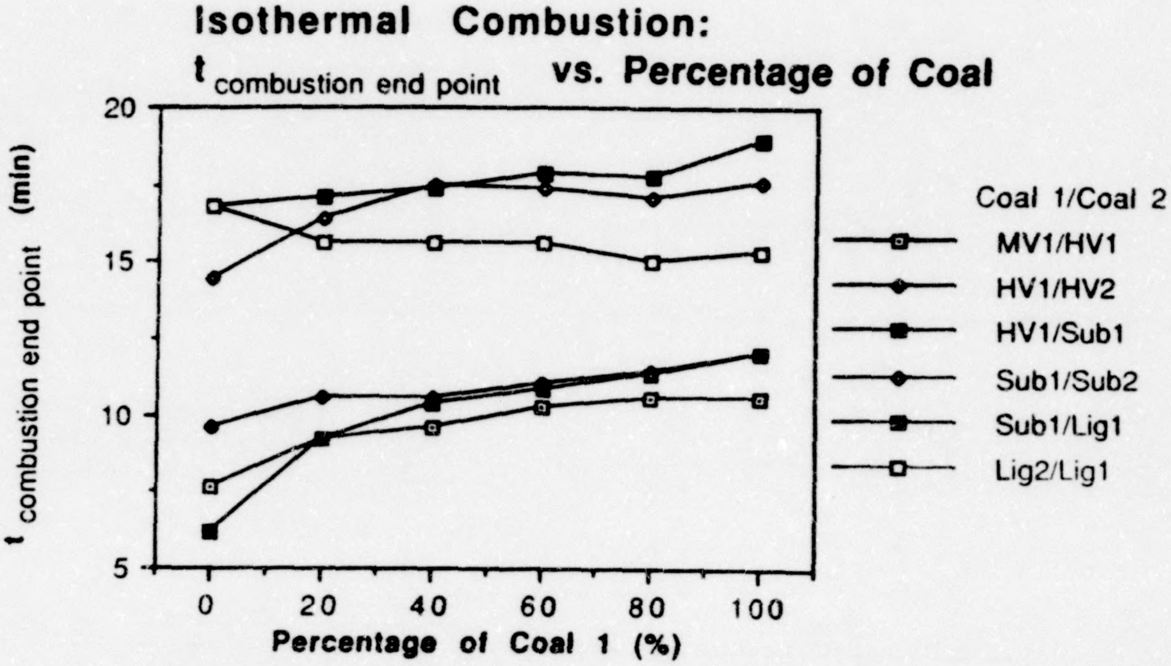

Figure 36. Isothermal Combustion - $t_{\text{combustion end point}}$ Values for Six Groups of Coal Blends.

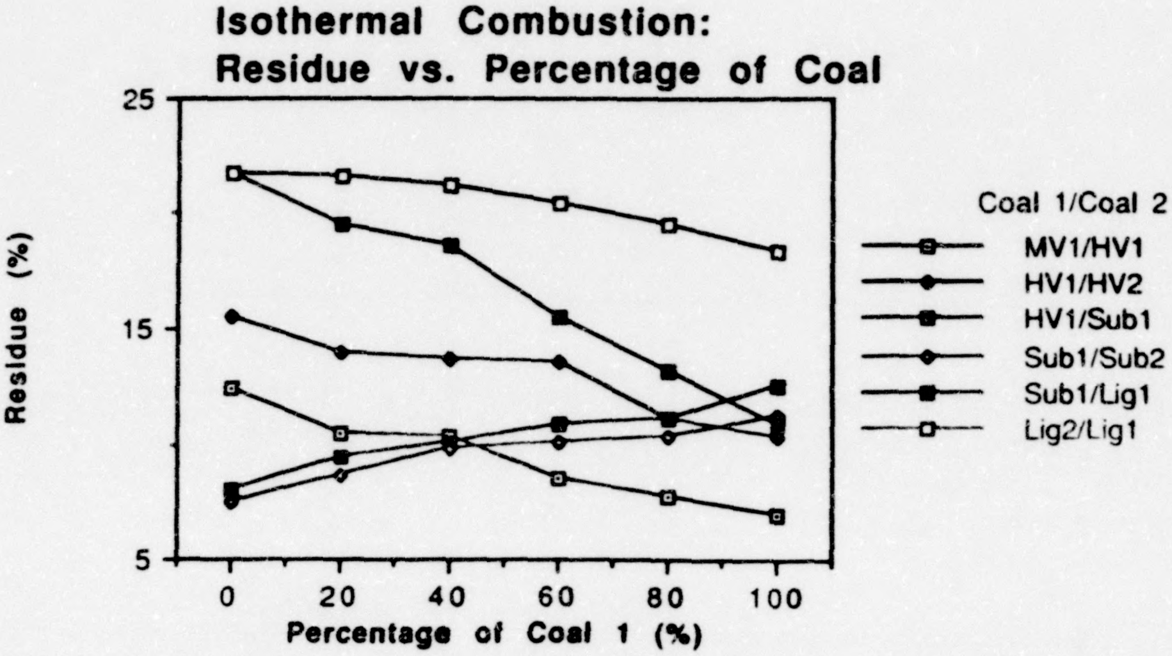

Figure 37. Isothermal Combustion - Residue Values for Six Groups of Coal Blends.

display nonadditive results for all coal blends. For example, for MV1 and HV1 coal blends, when the MV1 content increased from 0% to 100%, the result was a decrease in the residue from 12.36% to 6.92%. The residue values for Lig1/Sub1, Lig2/Lig1 coal blends did not clearly exhibit a nonadditive trend. In Figures 35-37, it should be noted that the Lig2/Lig1 coal blends did not show an additive or a nonadditive relationship clearly. This circumstance may be due to the similarity in coal rank of Lig1 and Lig2. Similar types of coal might have similar ingredients of mineral matter which results in a lower mixed catalyst effect.

The nonadditive nature of the coal blend samples may be due to the mixed catalysts effect (synergism). In general, when two type of catalysts are mixed with different proportions, the amount of products, the content of products, and the mechanism of the reaction may be changed nonadditively (60-62). Therefore the mixed catalysts plays an important nonadditive role in all of the mechanistic and kinetic parameters of the reaction.

However, as the severity of the pyrolysis or reaction conditions increase, the metals lose their catalytic activity due primarily to a loss of dispersion via sintering. This occurs as the holding time at a certain temperature or the reaction temperature itself increases (63). It is also a nonadditive effect for the reaction temperature. Thus, the temperature also plays a second important role in the process of coal pyrolysis and combustion.

From the results of these experiments, we find that sometimes the parameters of two individual coal samples are quite close. Therefore it is difficult to find additive or nonadditive relationships for the parameters of their blends. This occurs as a result of the differences in the parameters being less than instrumental deviations. Thus we put more weight on the coal blend results which show a greater difference in their parameters.

CONCLUSIONS

Some important conclusions desired from this study are:

1) TGA is a useful analytical procedure for coal blends. The procedure is simple, rapid and yields precise, reproducible results.
2) Based on the TG curves, TG parameters such as T_{max}, R_{max}, T_i and $T_{1/2}$ are nonadditive for coal blends; weight loss between 220 °C and 700 °C is additive for coal blends under non-isothermal pyrolysis conditions.
3) Based on the TG curves, some of the TG parameters under non-isothermal combustion conditions (residue, dry basis W.L.) and isothermal combustion conditions (t_{max}, R_{max}) are additive for coal blends. Other TG parameters under non-isothermal combustion conditions (T_{max}, R_{max}, T_i) and isothermal combustion conditions ($t_{break\ point}$, $t_{combustion\ end\ point}$, residue) are nonadditive.

Some recommendations for future work would be to:

1) Obtain quantitative results of the gaseous products evolved using TGA-GC.
2) Study the coal blends made by three individual coals under isothermal and non-isothermal processes using pyrolysis and combustion conditions to see if there is a trend towards either additive or nonadditive results.

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