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A STUDY OF THERMAL ANALYTICAL VALUES FOR COAL BLENDS BURNED IN AN AIR ATMOSPHERE *

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ABSTRACT

This study was aimed at providing a rapid and reliable method for predicting the performance of coal blends burned in industrial furnaces. The variation in certain coal blend parameters (such as T_{max}, and R_{max}), obtained by thermogravimetric analysis (TGA) were examined and compared with values of coal mixtures evaluated from the following general expression (linear additive rule)

$M = (1 - x)M_a + xM_b$

where M represents the composite value of any of the parameters investigated, and x is the weight fraction of component b in the mixture. The TGA was operated in both the programming and isothermal modes to provide a wide range of sample heating rates. The results obtained were dependent on the sample heating rate: for the runs in the programming mode (low sample heating rates, not exceeding 100 °C min^{-1}) experimental values of T_{max}, R_{max} and T_i for the coal blends did not follow the above equation, suggesting a non-additive relationship. When the isothermal mode was used (average sample heating rates up to 500 °C min^{-1}) values of $t_{\text{break point}}$, $T_{\text{combustion end-point}}$, and the residue for the blends did not follow the additive relationship.

INTRODUCTION

The cost and availability of coals with desired properties are a principal economic consideration. Generally, the quality of coal or blended coal is assessed on the basis of certain parameters associated with the pyrolysis and combustion process [1]. The current practice for determining the overall quality of blended coals is to use the weighted average values for the individual coals in the blend [2–5]. This approach may give accurate composite values for moisture content, total sulfur, and coal heating value of

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a coal blend, but not for volatile matter and ash contents. However, it has been shown that the calculated composite values for other coal blend parameters, such as the Hardgrove grindability (HGI), ash fusibility, and free-swelling index (FSI), are not reliable. These parameters do not represent the properties of a blended coal sample [6–10].

The aim of the present study was to establish whether the linear additive rule (eqn. (1))

$$M=(1-x)M_a+xM_b \tag{1}$$

is applicable to a number of coal blend parameters obtained using a thermogravimetric analyser. Several TGA parameters were selected: T_{max}, the temperature at the point where the mass-loss rate is maximum (°C); R_{max}, maximum rate of weight-loss divided by the initial weight of burnable material (% min^{-1}); T_i, initial decomposition temperature (°C); $T_{combustion\ end\text{-}point}$ (°C); $t_{break\ point}$ (min); and the residue (%).

Parameters obtained in such laboratory-scale experiments have been used in the past to predict the relative performance of coal in large furnaces. The results of this study are expected to provide a rapid and inexpensive test for rating coal blends.

EXPERIMENTAL

Materials

The coals which were used to prepare the blends are identified in Table 1. The coals were analysed for a number of properties (Table 2): ultimate

TABLE 1

Coals used in the study

Coal No.	Rank [a]	Source
86027	LigA	PRPS Coal, Saskatchewan, Canada
85091	LigA	BDPS Coal, Saskatchewan, Canada
86039	SubB	Jacob's Ranch Mine, Wyoming, U.S.A.
82045	SubC	Belle Ayr Mine, Wyoming, U.S.A.
86046	hvAb	Poplar Lick Mine, Bell Co., Kentucky, U.S.A.
85099	hcBb	WKy #12, Muhlenberg Co., Kentucky, U.S.A.
86026	mvb	Consolidation Coal Co., Pennsylvania, U.S.A.

[a] Apparent rank using as-determined moisture values.

TABLE 2

Analytical values of coals

Parameter [a]	Coal No.						
	86027	85091	86039	82045	86046	85099	86026
Moisture (%)	17.95	18.39	15.24	16.04	2.03	5.92	1.07
Ash (%)	18.89	15.10	8.27	5.78	10.81	15.15	6.03
Vol matter (%)	41.0	39.5	44.1	43.2	38.4	35.7	25.3
Carbon (%)	55.31	59.42	66.78	67.95	73.87	64.55	84.36
Hydrogen (%)	3.33	3.57	4.60	4.22	5.06	4.03	4.55
Nitrogen (%)	0.38	0.96	0.97	0.93	1.57	1.37	1.08
Sulfur (%)	0.73	0.34	0.64	0.36	0.89	3.78	0.85
Btu/1b	8767	9612	11434	11340	13186	11421	14668
HGI	35	34	40	41	40	50	90
FSI	0	0	0	0	4.0	1.0	9.0

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

TABLE 3

Elemental composition of ashes from coals

Metal oxide	Coal No.						
	86027	85091	86039	82045	86046	85099	86026
SiO_2 (%)	41.14	44.88	35.47	33.05	50.43	45.47	8.62
P_2O_5 (%)	0.63	0.45	1.31	1.50	2.36	0.20	0.01
SO_3 (%)	7.84	5.66	10.54	9.26	1.08	0.72	7.99
K_2O (%)	1.60	1.02	0.48	0.16	1.91	2.63	1.34
CaO (%)	13.21	13.15	18.48	26.9	2.71	0.55	9.26
TiO_2 (%)	0.82	1.07	1.12	1.25	1.66	1.00	1.18
Fe_2O_3 (%)	4.20	3.49	6.25	5.57	5.32	24.14	12.25
Na_2O (%)	0.92	0.72	1.20	1.04	0.63	0.51	0.79
MgO (%)	1.40	1.20	3.27	4.59	1.06	1.07	1.61
Al_2O_3 (%)	23.16	21.36	16.69	14.70	24.51	19.22	24.72

TABLE 4

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 volume bitumen (86039 + 86046)
5	2 High volume bitumen (86046 + 85099)
6	High volume bitumen + medium volume bitumen (86046 + 86026)

analysis, proximate analysis, gross heating value, HGI, and FSI. The ash composition of the blends is given in Table 3.

Sample preparation

A series of six coal blends were prepared using seven air-dried coals, size-reduced to -8 mesh (2.4 mm). The combinations of the coals used for making the binary blends are shown in Table 4. Each blend was mixed in four different component ratios (20, 40, 60 and 80%). There were 24 different samples of blended coal in all; about 1000 g of each of the blended coal samples was further size-reduced to -60 mesh, for the thermogravimetric analysis (TGA) studies. All coal samples and blends were prepared by the Coal and Fuel Characterization Laboratory at Western Kentucky University.

TGA conditions

The combustion behavior of coal blends was studied using a DuPont 951 TGA instrument in both the isothermal and programming heating modes. The atmosphere used for the study was air [11]. For the runs using the programming mode, the sample was heated at 20 °C min^{-1} from 30 °C to a maximum temperature of 750 °C. For the isothermal mode, as soon as the set maximum temperature was reached, the sample pan was moved into the hot furnace and left for 30 min. to ensure that the coal sample was completely ashed.

In order to determine the break point for each coal sample, the isothermal temperatures were set according to the rank of a coal blend. This was necessary to ensure that the TGA results would show, for every run, the break points and combustion end-points. For example, the TGA maximum furnace temperature was set at 600 °C for MV1 and HV1 coal blends. A lower temperature of 550 °C was for HV1 and HV2, HV1, and Sub1 coal blends, and 400 °C for Sub1 and Sub2, Sub1 and Lig1, Lig1 and Lig2 coal blends. Using 600 °C for the low-rank coal blends resulted in a fast rate of coal decomposition so that the break point was not observed. The high-rank coal blends did not decompose completely when the maximum TGA furnace temperature was set at 400 °C. The temperature was too low, so that the combustion end-point was not observed within the allotted decomposition time.

From the TG plots of weight-loss vs. temperature (programming mode) or time (isothermal mode), the following thermal parameters were determined: T_{max}, R_{max}, T_{i}, weight-loss, $T_{1/2}$, residue, $t_{\text{break point}}$, and $t_{\text{combustion end-point}}$. Table 5 summarizes the maximum relative standard deviation for the coal samples: this was 3% for temperature measurements, 4% for weight measurements, and close to 6% for time measurements. These maximum relative standard deviations were used to define the allowed maximum relative

TABLE 5

Maximum relative standard deviations for parameters

Combustion parameter	Maximum relative standard deviation (%)
Temperature	
T_{max}	1.9
T_i	2.3
Weight	
R_{max}	3.9
Weight loss	2.0
Residue	3.7
Time	
t_{max}	5.6
$t_{break point}$	3.7
$t_{combustion end\text{-}point}$	2.0

errors, for the determining the additive or nonadditive relationships. Thus variations in values of the experimental parameters, from the linear additive rule, within the error band were considered insignificant.

RESULTS

Thermogravimetric curves

Typical thermogravimetric (TG) curves for the two coal blends are shown in Figs. 1 and 2. The first set of figures represent TGA results obtained using the programming mode, whereas the second set was obtained using the isothermal mode. The major decomposition stage (major peak on the DTG curve) was observed for all the coal blends studied.

Programming mode (low heating rate)

Five kinetic parameters obtained from the TG curves are discussed in this section. The results concerning the additivity or nonadditivity of these thermal parameters for coal blends are summarized in Table 6.

Initial decomposition temperature, T_i

T_i was defined as the temperature at which the rate of weight loss was 1% min^{-1}. Figure 3 presents the T_i values for the coal blends. The values of T_i for coal blends HV1/Sub1 were nonadditive because several of the points fell outside the allowed error range of 3% (see Table 7). The nonadditive relationship was expected because the T_i values for HV1 and Sub1 were very different.

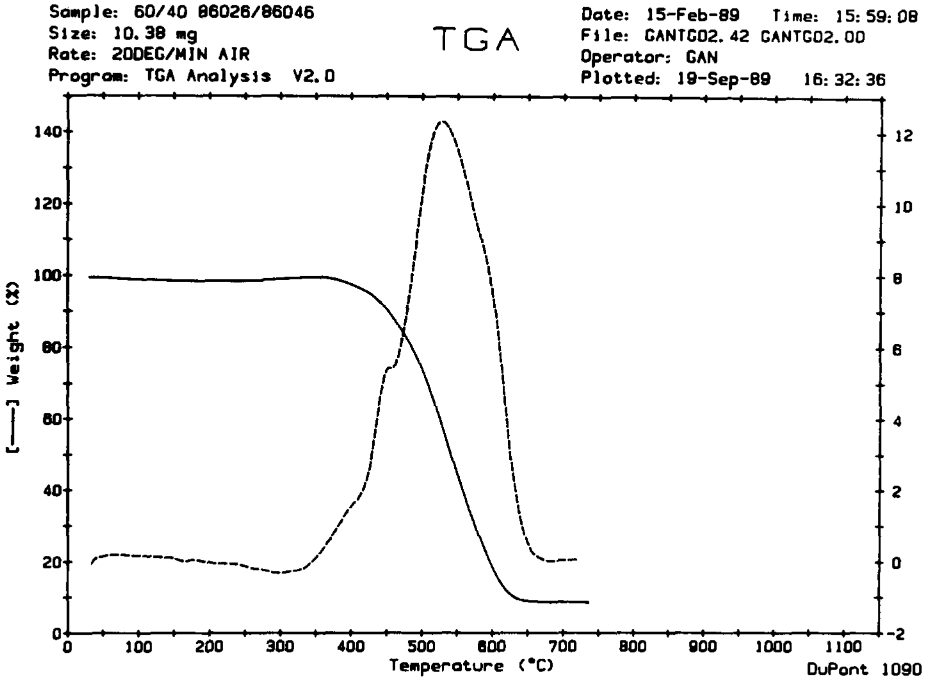

Fig. 1. TG heating curve: 60% MV1 + 40% HV1 coal blend in air under isothermal conditions.

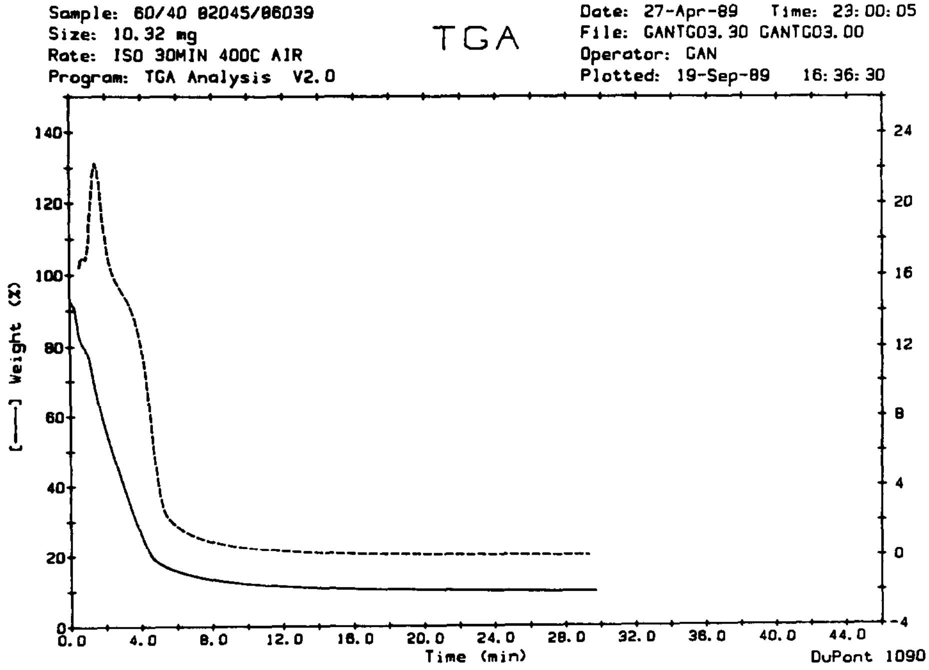

Fig. 2. TG heating curve: 60% HV1 + 40% Sub1 coal blend in air under isothermal conditions.

TABLE 6

Relationship of parameter values for each set of coal blends: programming mode

Parameter	Relationship type		
	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

Values for the other coal blends HV2/HV1, MV1/HV1, Sub1/Lig1, Sub1/Sub2 and Lig2/Lig1 did not show a definite non-linear relationship. For Lig1 and Lig2 coal blends, when the Lig2 content was increased from 0 to 100%, T_i remained almost constant.

Temperature of maximum rate of weight loss, T_{max}

The values of T_{max} for coal blends HV1/Sub1 were also nonadditive because several of the T_{max} values were located outside the allowed error

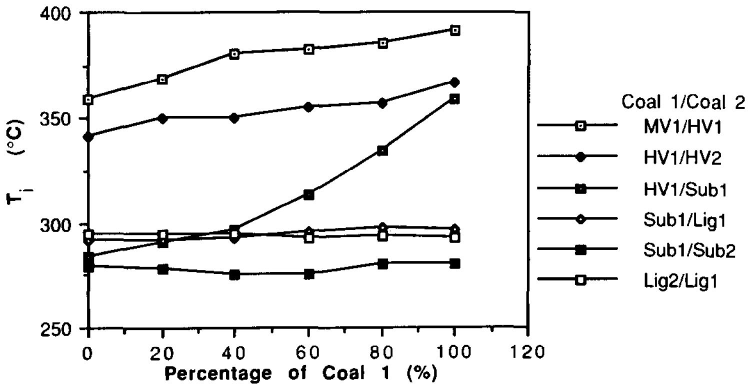

Fig. 3. Programming mode: T_i values for six groups of coal blends.

TABLE 7

Comparison of T_i results from experiments and predictions

Coal blend HV1/Sub1	T_i (°C)		Relative error (%)
	Experimental	Predicted [a]	
0%/100%		280	
20%/80%	290	294	1.4
40%/60%	297	308	3.6
60%/40%	310	322	3.7
80%/20%	330	336	1.8
100%/0%		350	

[a] From linear additive rule (eqn. (1)).

range for an additive relationship. However, the values of T_{max} for coal blends like Sub1/Sub2 and Lig2/Lig1 was insignificantly changed with mixture ratio in the blend. The results for this parameter are plotted in Fig. 4.

Reactivity at T_{max}, R_{max}

The values of R_{max} for coal blends HV1/Sub1, MV1/HV1, Lig2/Lig1 and Sub1/Sub2 were nonadditive. However, for coal blends Sub1/Lig1 and HV1/HV2, R_{max} did not vary with component concentration in the blend as illustrated in Fig. 5. The remaining blends did not display characteristics of an additive coal sample. Some differences were quite large, especially in blends involving low-rank coals. This was especially true of blends made up of HV1 and Sub1 coals.

Dry basis weight loss between 220 and 750 °C

The values of weight loss (WL) (dry basis) for coal blends MV1/HV1, Sub1/Sub2, Sub1/Lig1 and Lig2/Lig1 were additive. The change in weight

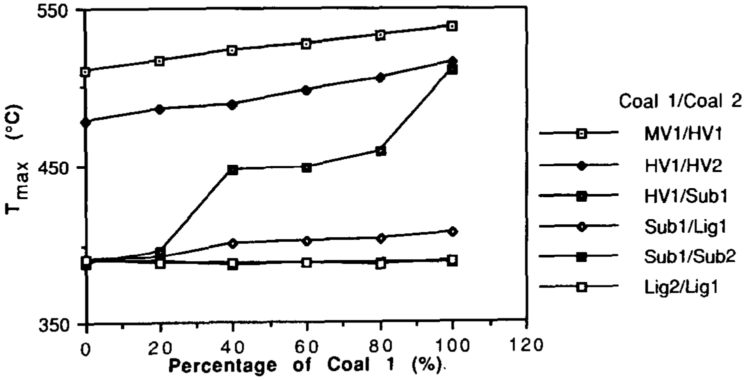

Fig. 4. Programming mode: T_{max} values for six groups of coal blends.

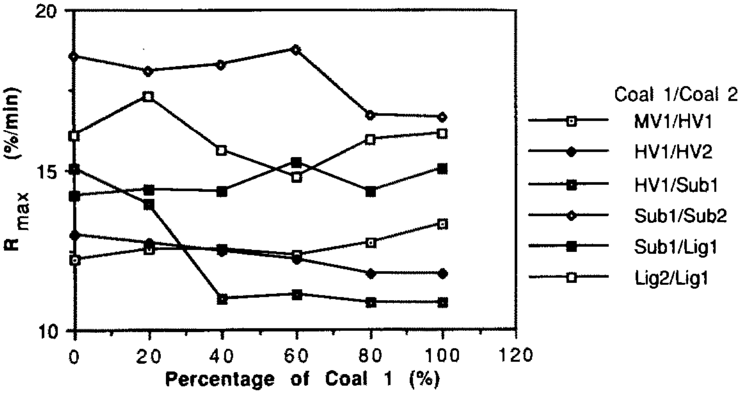

Fig. 5. Programming mode: R_{max} values for six groups of coal blends.

loss was significant for these coals. For example, for blends made up of MV1 and HV1 coals the WL (dry basis) increase from 88.7 to 95.84% when the MV1 content was increased from 0 to 100%. However, for HV1 and Sub1 coal blends, when HV1 content was increased from 0 to 100% the WL (dry basis) remained close to 90%, because in this case the WL (dry basis) values of HV1 and Sub1 were very close. (See Fig. 6.)

The WL (dry basis) and residue values were nonadditive. 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 not toal WL.

Residue

The residue is the material which remains after the sample has been burned to completion. Figure 7 shows the results for the coal blends as a function of component composition. The residue for MV1/HV1 and for Lig1/Sub1 coal blends was nonadditive. The residue was significantly

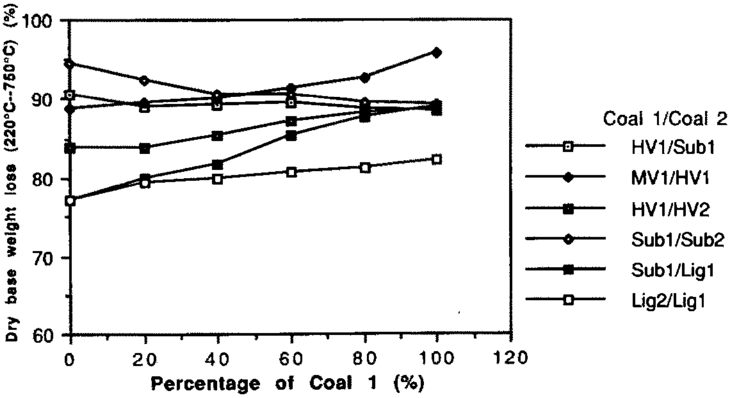

Fig. 6. Programming mode: dry basis weight loss values for six groups of coal blends.

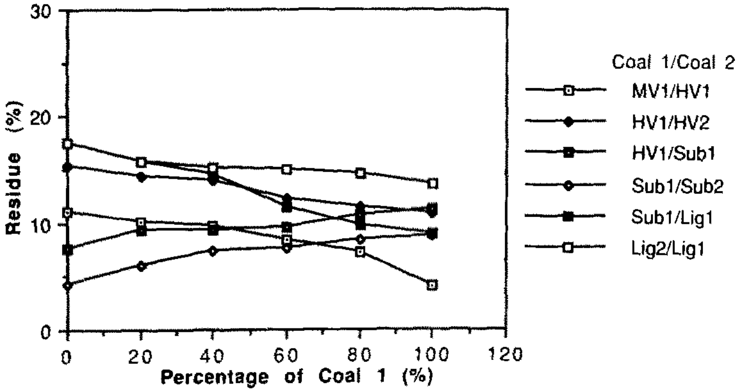

Fig. 7. Programming mode: residue values for six groups of coal blends.

different for the individual coals in each of these mixtures. For example, in the case of HV1 coal the residue was 11.3% and for MV1 coal it was 6.46%.

Isothermal mode (intermediate heating rates)

Figure 2 shows the TG heating curve for a coal blend decomposed in the isothermal mode. The same five kinetic parameters studied using the programming mode were investigated in the isothermal mode in order to evaluate the effect of using higher heating rates. The results are summarized in Table 8.

Time of maximum rate of weight loss, t_{max}

The values of $t_{\max}$ for coal blends MV1/HV1 and HV1/Sub1 showed an additive relationship. All the points were located within the allowed error range. Plots of these experimental points are shown in Fig. 8.

At low heating rates the values of $T_{\max}$ for coal blend HV1/Sub1 were nonadditive unlike the case here. Such results point to the importance of the heating rate on results concerning coal blends.

The $t_{\max}$ values for most coal blends, such as HV1/HV2, Sub1/Sub2, Sub1/Lig1, and Lig2/Lig1, appeared to be almost constant. The values for individual coals were generally very close at around 1.40 min.

Reactivity at T_{max}, R_{max}

The values of $R_{\max}$ for coal blends MV1/HV1, Lig2/Lig1 and HV1/Sub1 were found to be additive. Once more increasing the heating rate provided compliance with the linear additive rule when this was not originally the case.

The $R_{\max}$ values for the individual coals, HV1 and MV1 were 32.0% $\min^{-1}$ and 17.6% $\min^{-1}$, respectively, and, therefore, $R_{\max}$ was sensitive to

TABLE 8

Relationship of parameter values for each set of coal blends: isothermal mode

Parameter	Relationship type		
	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

variations in mixture composition. This was not the case for a number of the blends shown in Fig. 9 which showed similar maximum reactivities.

For the runs in the isothermal mode, sample temperature played a more important role than the catalytic effect, which is a function of the mineral content of a coal. This may explain why there was better agreement with the linear additive rule in this anode. The values of t_{max} and R_{max} were determined close to the beginning of the heating cycle, after a lapse of about

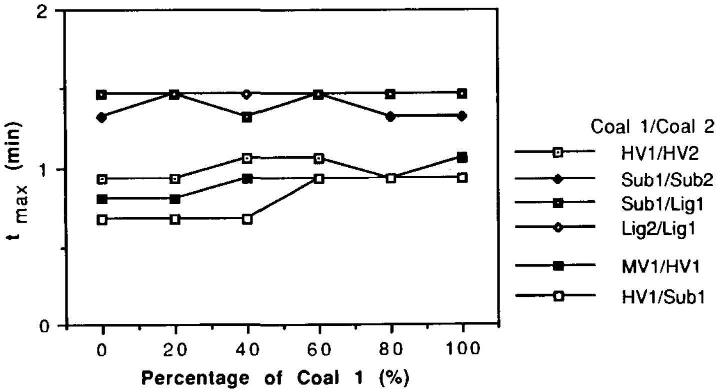

Fig. 8. Isothermal mode: t_{max} values for six groups of coal blends.

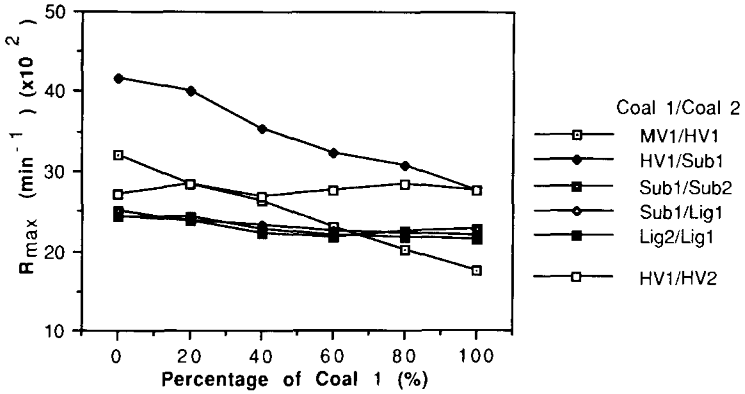

Fig. 9. Isothermal mode: $R_{\max}$ values for six groups of coal blends.

2 min. At this time the coal sample would not have reached the set furnace temperature; this may be referred to as the sample heating stage. The catalytic effect of the minerals in the coal was more significant at the low heating rate, because $R_{\max}$ occurred after a longer decomposition time and at a higher temperature.

$t_{break\ point}$

The break point is located where the rate of change of reactivity, R, is maximum. Plots for this parameter are given in Fig. 10. The value of $t_{\text{break point}}$ for most coal blends HV1/HV2, HV1/Sub1, and Sub1/Sub2 was nonadditive. The experimental values fell outside the allowed error range for an additive relationship, because this parameter is measured in the region where the catalytic effect of the minerals becomes important. Since the ranks of Lig1 and Lig2 are very close, the $t_{\text{break point}}$ values for Lig1, Lig2, and their blends did not show any significant differences.

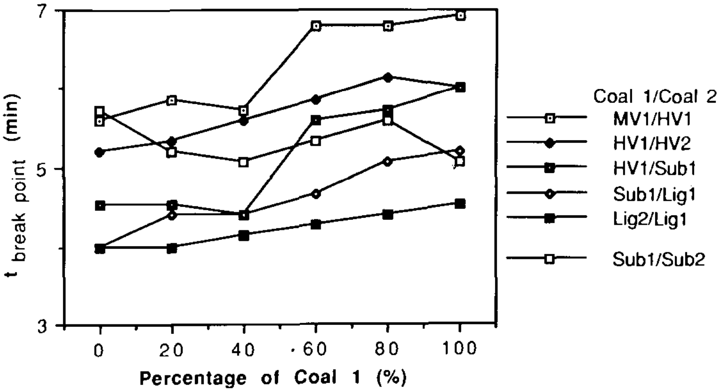

Fig. 10. Isothermal mode: $t_{\text{break point}}$ values for six groups of coal blends.

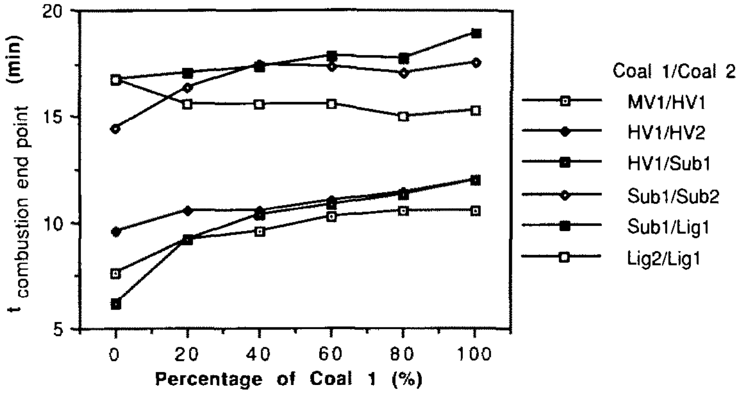

Fig. 11. Isothermal mode: $t_{\text{combustion end-point}}$ values for six groups of coal blends.

$t_{\textit{combustion end-point}}$

This parameter was nonadditive for most coal blends, especially for the HV1/Sub1 coal blend. Only a few experimental points fell within the allowed error range for an additive relationship (Fig. 11). These results may be attributed to a mixed-catalyst effect when the reaction speed was decreased in some cases to a low value of 0.1% min^{-1}.

Residue

Calculated values of the residue using the linear additive rule for HV1/HV2, MV1/HV1, HV1/Sub1 and Sub1/Sub2 coal blends did not agree with those obtained experimentally for the respective blends. This confirmed the existence of a nonadditive relationship. Figure 12 shows a plot of the experimental points.

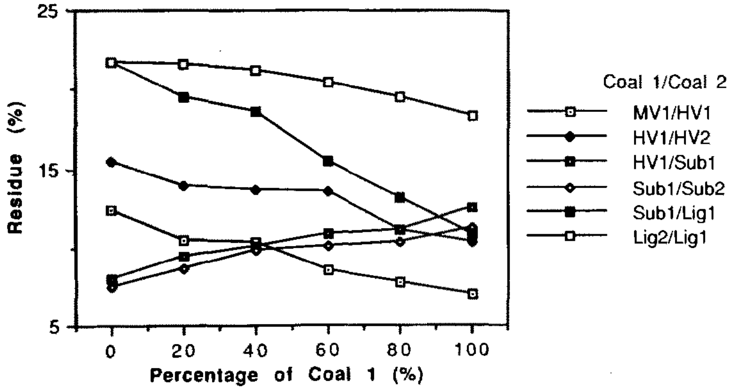

Fig. 12. Isothermal mode: residue value for six groups of coal blends.

DISCUSSION

A number of important kinetic parameters were investigated at low and intermediate heating rates. The nonadditive nature of the coal-blend samples was attributed in several instances to the effect of minerals in coal, i.e. a mixed-catalyst effect (synergism). In general, when two types of catalyst are mixed in different proportions, the amount of products, the content of products, and the mechanism of the reaction may be changed nonadditively [12–14]. Therefore, the mixed catalyst plays an important nonadditive role in all 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 [15]. This condition is unlikely to be reached in the present study.

For some of the parameters, the effect of catalyst was not important as was the case for R_{max} obtained in the isothermal mode. The results observed were attributed to a temperature effect, which influenced the process of coal pyrolysis and combustion.

In some cases the parameters determined experimentally for individual coal samples were quite close. When this occurred, it was difficult to know for sure whether the relationship for these parameters, for the coal blends was additive or nonadditive. Therefore, only the results for blends made up of coals having significantly different parameters were considered to be reliable.

CONCLUSIONS

Several points may be made concerning the suitability of the linear additive rule for the coal blends investigated in this study.

For the runs in the programming mode (low sample heating rates): the residue (dry basis WL) could be predicted using the linear additive rule; and T_{max}, R_{max}, and T_{i} could not be predicted using the linear additive rule.

For the runs in the isothermal mode (intermediate sample heating rates): t_{max} and R_{max} could be predicted using the linear additive rule; and $t_{\mathrm{break\,point}}$, $t_{\mathrm{combustion\,end\text{-}point}}$, and residue could not be predicted using the linear additive rule.

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