COAL ANALYSIS USING THERMOGRAVIMETRY *

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ABSTRACT

Thermogravimetric analysis is being used increasingly today to obtain kinetic data related to coal decomposition. However, this method is open to criticism on the basis that the meaning of the activation energy of solid state reactions obtained from TG experiments is not clear. In this study a linear relationship between procedural activation energy and heat of reaction is developed. This is typical of elementary reactions of atoms and small radicals. The effects of alkali metal salts on the decomposition of coal under three gas atmospheres (N_2, CO_2 and air) are investigated. Several features are reported such as the effect of the catalysts on coal conversion and CH_4, CO and CO_2 emission. These are related to observed changes in activation energy.

INTRODUCTION

With the recent reemphasis on coal as an important source of energy, numerous studies have appeared on the acceleration of coal gasification and the improvement of combustion efficiency [1,2]. This paper reports the results of an investigation into the effects of alkali carbonates and chlorides on the catalytic decomposition of a subbituminous coal in nitrogen, air, and carbon dioxide. Thermogravimetric analysis and differential thermal analysis were used to characterize the mass loss and heat of reaction, respectively. These thermal analytical techniques are increasingly being used today because of their high precision and rapidity of obtaining results. However, kinetic parameters obtained using such methods vary with experimental conditions, e.g., heating rate [3], and are, therefore, controversial.

The objectives of this investigation are:

(1) to document the influence of furnace atmosphere on the catalytic effect of alkali metal salts;

(2) to determine the effects of mixed catalysts of the same group as opposed to the effects of a single catalyst;

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* Paper presented at the 185th National ACS Meeting.

(3) to provide insight into the meaning of the measured activation energy.

Attention has been directed to determining the different activation energies along a thermogram as well as defining the temperature zones of methane, carbon monoxide, and carbon dioxide emission. The experimental activation energy was compared to the measured heat of reaction and to the mass-loss of coal. The mass of carbon dioxide and carbon monoxide produced during combustion was calculated to reflect the effect of the catalysts on combustion efficiency and pollution, respectively.

THEORETICAL MODEL

To describe the rate of mass loss of coal the following equation was used [4,5]

$$\frac{-1}{m_i - m_f} \frac{dm}{dt} = A \exp\left(\frac{-E}{RT}\right)\left[\frac{m - m_f}{m_i - m_f}\right] \tag{1}$$

This equation assumes the following:

(a) the rate of coal conversion, dC/dt, equals $k\, f(C)^n$ where k is a rate constant, n is the reaction order and $C = 1 - [(m - m_i)/(m_i - m_f)]$;

(b) the rate constant, k, obeys the Arrhenius Law;

(c) the reaction is first order ($n = 1$);

(d) the pre-exponential factor, A, in the Arrhenius Law is independent of temperature.

The activation energy, E, measured in this experiment is an apparent activation energy and because it is dependent on the heating rate amongst other factors it should be understood to be an apparent procedural-activation energy.

EXPERIMENTAL

The coal used in this investigation was subbituminous Inland-Mine coal (-270 and $+325$ U.S. mesh) the same as that used in a previous study [3]. The properties of the coal are given in Table 1. The catalysts Li_2CO_3 (Research Organic/Inorganic Chemical Corp.), Na_2CO_3 (J.T. Baker Chemical Co.), K_2CO_3 (Fisher Chemical Co.), and NaCl and KCl (Mallinkrodt Inc.) were certified grade. Studies of the reactivity of coal in the presence of the alkali metal salts were performed using thermal analytical techniques. Measurement of mass-loss (TG) and rate of mass-loss (DTG) vs. temperature (or time) were made using a DuPont 951 thermogravimetric analyzer (TGA) in the range 283–1223 K and a linear heating rate of 20°C min^{-1}. The atmospheres used were oxygen-free nitrogen, extra dry air, and carbon dioxide each flowing at 50 ml min^{-1} at S.T.P. (all Matheson Co.). An oxygen

TABLE 1

Composition of inland-mine coal (mass %)

	As received	Dry basis		As received
Proximate analysis			*Ultimate analysis*	
Moisture	5.2	—	Moisture	5.2
Fixed carbon	54.0	57.0	Carbon	60.4
Volatiles	32.0	33.7	Hydrogen	4.5
Ash	8.8	9.3	Nitrogen	1.7
	$\overline{100.0}$	$\overline{100.0}$	Sulphur and oxygen	not determined
			Ash	8.8
			C/H	1.1
			C/N	41.4

trap was introduced into the system when nitrogen was used as the gas atmosphere to ensure the removal of any traces of oxygen. An evaluation of the TGA's performance is given elsewhere [3].

The heat of reaction was measured using a DuPont differential thermal analyzer (DTA) with a 1200°C cell. The DTA analyses were also performed under the same linear heating rate of 20°C min^{-1} and gas flow rate of 50 ml min^{-1}. The above operating conditions were chosen on the basis of a previous study [3] on the effects of heating rate and furnace atmosphere on the decomposition of the same coal.

Gas analysis was performed using a Perkin-Elmer infrared spectrophotometer (Model 735B). The frequencies 2350, 2160, and 1300 cm^{-1} were selected to detect for CO_2, CO, and CH_4, respectively. These values were chosen as a result of experiments performed using certified standard gases.

RESULTS

To compare the catalytic effects of the set of Group 1A additives on the decomposition of coal, the amount of lithium, sodium, and potassium salts added to the coal was calculated on the basis of a fixed amount of metal ion (i.e., 1 mg-atom per g of coal) rather than on a mass basis. The rate of mass loss of the coal (on a dry basis) between 283 and 1223 K is plotted in Figs. 1 to 3 for different furnace atmospheres. The range of evolution of CO, CO_2, and CH_4 is marked using broken and solid lines. The solid lines indicate an amount of gas $\geqslant 0.02$ mg.

The differential thermogravimetric curve exhibits three zones (peaks) in the case of nitrogen (Fig. 1). Zone I represents the evolution of water and occurs below 523 K. Zone II covers the temperature range 523–938 K. Compounds containing carbon, hydrogen, and oxygen are released as a result of reactions of the functional groups. This is termed the primary
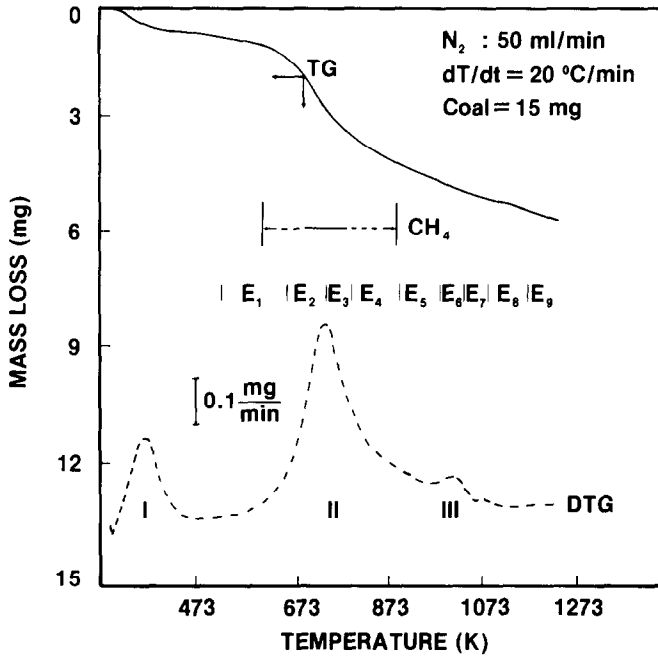
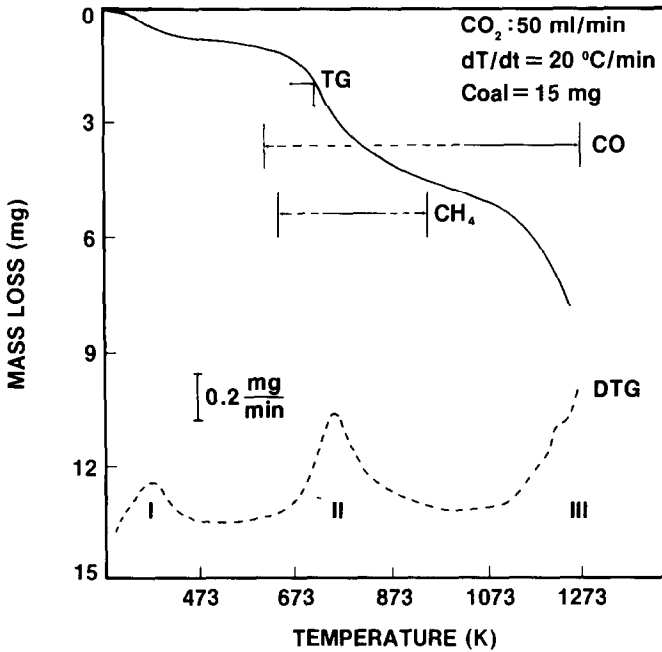Fig. 1. Thermogravimetric heating curves for coal in nitrogen (10^5 N m^{-2}).

Fig. 2. Thermogravimetric heating curves for coal in carbon dioxide (10^5 N m^{-2}).
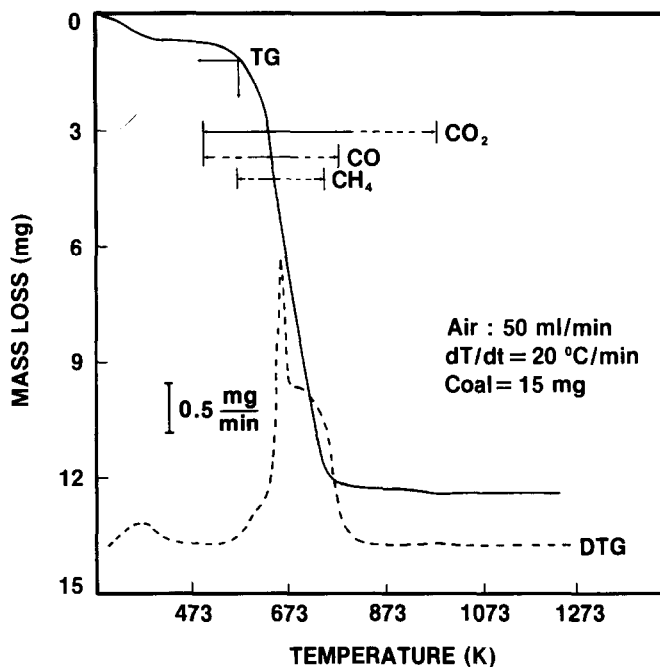
Fig. 3. Thermogravimetric heating curves for coal in air (10^5 N m^{-2}).

devolatilization range. Zone III contains the second decomposition range in which mostly methane and hydrogen are evolved [6]. Only an analysis for methane was performed in the case of nitrogen. According to Fig. 1, most of the CH_4 appeared in zone II rather than in zone III. (The solid line in Fig. 1 indicates the presence of methane in amounts $\geqslant$ 0.02 mg.) Such results agree with those of Jüntgen and Van Heek [6a].

Figure 2 shows the decomposition of the same coal in a carbon dioxide atmosphere. Similar zones to those present in the case of a nitrogen atmosphere were observed. However, the rate of reaction in zone III has been greatly increased. Judging from the relatively small amounts of carbon monoxide produced in the primary decomposition stage (zone II) CO_2 has the effect of an inert gas. It is only in zone III that the $C + CO_2$ reaction becomes important as indicated by the solid line where carbon monoxide concentration is $\geqslant$ 0.025 mg. However, the reaction was not completed within the experimental time (temperature range) investigated as is indicated by the DTG curve in Fig. 2.

In the presence of air, coal decomposition was much more rapid, as expected. Because of the high rate of the $C + O_2$ reaction (sharper DTG peaks) the main stages of decomposition, i.e., zones II and III, merged (Fig. 3). The reaction was completed in a much shorter time. In fact, the coal was reduced to a white ash at 920 K.

INFLUENCE OF THE ADDITIVES ON KINETIC PARAMETERS

In order to compare the effects of the alkali metal salts on the kinetic parameters, the activation energy along each thermogram was determined from plots of rate of mass-loss against the inverse of the absolute temperature. This defined the temperature region of constant activation energy. There were five such regions in the case of carbon dioxide compared to eight and nine in the case of air and nitrogen, respectively. The first four regions for coal in air are shown in Fig. 4. The first region is coded as E_1, the second as E_2, etc.

The TGA results indicate that in a nitrogen atmosphere the additives first reduce and then promote the decomposition of the coal (Fig. 5). The decrease in mass-loss of coal occurred in zone II (523–938 K) and was accompanied with a corresponding decrease in activation energy which
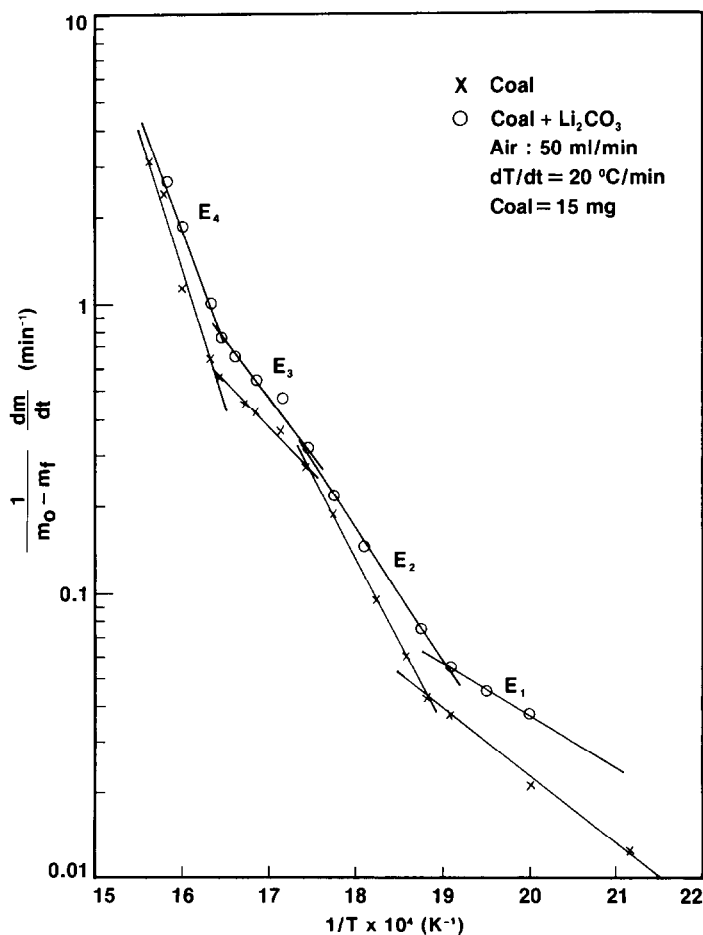

Fig. 4. Effects of the addition of Li_2CO_3 on the decomposition rate of coal in air.
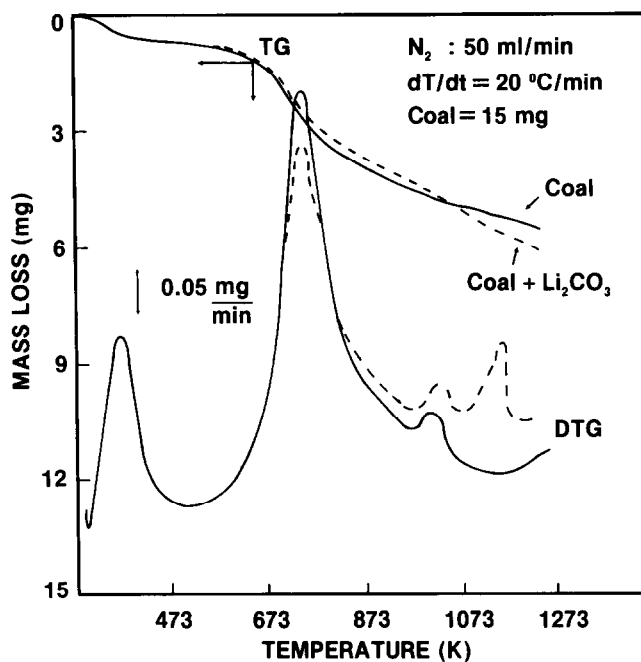
Fig. 5. Effect of Li_2CO_3 on the catalytic decomposition of coal in nitrogen (10^5 N m^{-2}).

TABLE 2

Selected activation energies

Additive	E_3 (kJ mol^{-1}) in N_2 [a]	E_{III} (kJ mol^{-1}) in N_2 [b]	E_6 (kJ mol^{-1}) in air [c]
Coal	50.2 ± 1.6	67.2 ± 2.3	6.2 ± 0.2
Coal + Li_2CO_3	31.8 ± 1.1	55.0 ± 1.8	11.7 ± 0.4
Coal + Na_2CO_3	46.2 ± 1.8	64.3 ± 2.3	9.7 ± 0.3
Coal + K_2CO_3	48.0 ± 1.2	57.0 ± 1.9	10.5 ± 0.4
Coal + KCl	42.9 ± 1.7	65.1 ± 2.3	9.5 ± 0.3
Coal + NaCl	—	—	9.6 ± 0.3

[a] 723–823 K. [b] 938–1223 K. [c] 670–680 K.

TABLE 3

Selected decomposition temperatures of coal and catalysts

Catalysts	Melting point (K)						
	From TG curve			From Weast [7]	Additive	Coal + additive	
	N_2	Air	CO_2		N_2	N_2	Air
Li_2CO_3	983	998	973	990	996	983	970
Na_2CO_3	1123	1123	1003	1124	1113	1099	1079
K_2CO_3	1148	1098	1098	1164	1160	1153	1148

occurred in the following order: coal $> K_2CO_3 > Na_2CO_3 > Li_2CO_3$ and $K_2CO_3 > KCl$ (Table 2). The lowering of the activation energy does not, therefore, reflect an increase in coal reactivity (i.e., conversion).

Above 983 K (zone III) the alkali metal salts began to melt (see Table 3). This altered the size of the temperature zones of constant activation energy and, therefore, a comparison of corresponding activation energy is meaningless. A weighted activation energy ($\bar{E} = \Sigma E_i \Delta C_i$) was, therefore, calculated for zone III (938–1223 K) and was found to be more suitable for the explanation of the catalytic effect of the additives (see Table 2). The activation energy of the catalyzed reactions thus calculated was in the order indicated, i.e., $Na_2CO_3 > K_2CO_3 > Li_2CO_3$. This was accompanied with an increase in the amount of coal devolatilized with Li_2CO_3 producing the greatest effect (Fig. 5). Therefore, in zone III the activation energy may be used to monitor the effect of a catalyst on coal reactivity. Although most of the mass loss occurred in zone II the mass change in zone III need only be considered to define the overall effect of a catalyst on coal conversion.

When nitrogen was replaced by air as the furnace atmosphere the effectiveness of the catalysts in reducing the activation energy of the coal reaction (also while increasing the mass-loss) was in the order $Li_2CO_3 > K_2CO_3 > Na_2CO_3$. This indicates that the presence of an oxidizing atmosphere does not influence the order of effectiveness of Li_2CO_3. The total region examined in Fig. 6 represents about 95% of the total amount of coal converted. This occurred at ~ 808 K which is below the melting points of the catalysts (Table 3). The values shown in Table 3 were obtained from TG and DTA experiments and are of the same magnitude as those provided in the literature [7]. The catalysts' melting points were, however, lowered in the presence of coal.

When the activation energy was measured along the thermogram in Fig. 3, it was observed that in two temperature zones, the additives increased the activation energy rather than decreased it (although the mass-loss was also increased). In this case the increase in activation energy also occurred in the above order (Table 2). However, K_2CO_3 produced a slightly higher level of
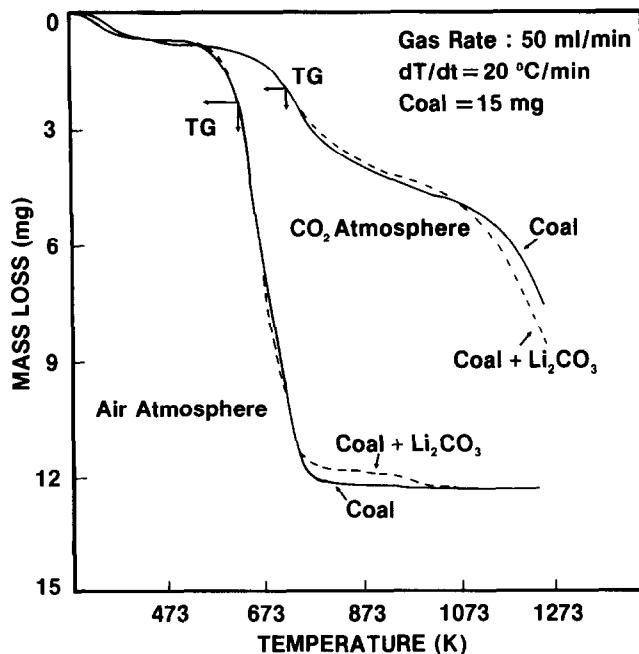
Fig. 6. Effect of Li_2CO_3 on the catalytic decomposition of coal in air and carbon dioxide (10^5 N m^{-2}).

conversion than Li_2CO_3. These conclusions are in agreement with a number of important studies on the decomposition graphite [8]; coal [9] and carbon black [10].

One of the objectives was to determine the effects of mixed catalysts of the same group as opposed to the effects of a single catalyst. Addition of a mixture of $Na_2CO_3 + Li_2CO_3$ to coal in a nitrogen atmosphere was next investigated. The result was a reduction of the previously observed inhibiting effect of the catalysts in the low temperature region. Therefore, a greater mass-loss occurred in this case than when equal amounts (atom/atom) of Na_2CO_3 or Li_2CO_3 were added. The mixed catalysts also promoted decomposition at the higher temperatures (zone III). They were also more effective when the experiment was performed in an oxygen atmosphere. The alkali chlorides were not discussed in detail because of their less important effects. However, a few of the results were included in Table 2 for comparison.

RELATIONSHIP BETWEEN HEAT OF REACTION AND ACTIVATION ENERGY

Addition of alkali metal salts to the coal reduced the heat of reaction (ΔH_R) under all atmospheres. In an air atmosphere, K_2CO_3 was found to
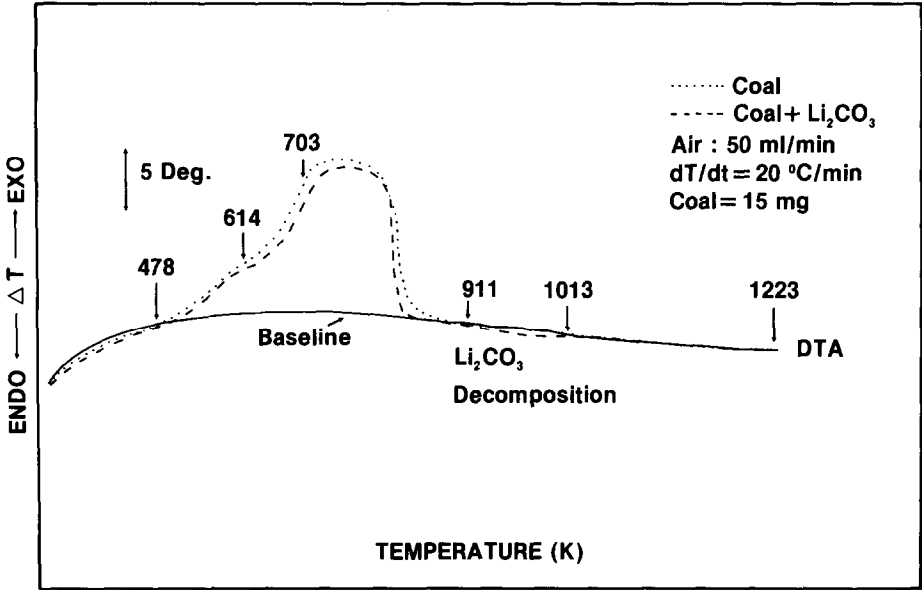
Fig. 7. DTA heating curve for coal and Li_2CO_3–coal mixture in air (10^5 N m^{-2}).

reduce ΔH_R more than Na_2CO_3; however, the order was reversed in a nitrogen atmosphere. Since Li_2CO_3 was found to have the greatest effect of the three catalysts it will be discussed in detail.

The effect of Li_2CO_3 on the decomposition of coal in air is shown in Fig. 7. (Above the melting point of $Li_2CO_3 \sim 911$ K, $\Delta H_R \approx 0$.) These additives
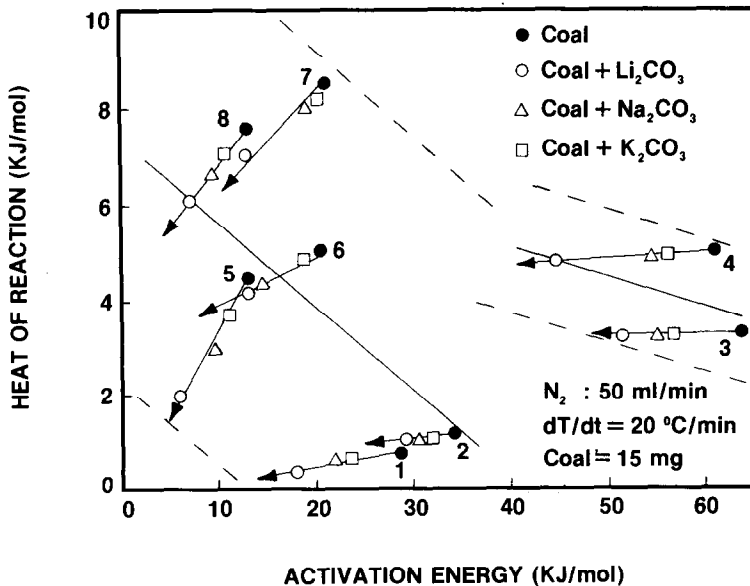

Fig. 8. Relationship between heat of reaction and activation energy in nitrogen (10^5 N m^{-2}).

also reduced the activation energy in the aforementioned order which explains the relationship found between activation energy and heat of reaction (Figs. 8 and 9). Every point in the plots represents a temperature interval of ~ 50°C at which a constant activation energy located on a TG curve was operative. These intervals were subsequently used to define the corresponding heat of reaction from DTA curves operated under similar conditions of gas atmosphere, gas flow rate, etc. The arrows indicate the effect of the catalysts within a given temperature interval. The change in ΔH_R was sometimes small as is indicated in regions 3 and 4 of Fig. 8 and in most regions of Fig. 9. The correlations between heat of reaction and activation energy were as follows: in N_2 for most of region II (see Fig. 8)

$$|\Delta H_R| = 7.18 - 0.166\ E, r^2 = 0.81 \tag{2}$$

in air for the temperature range (473–698 K) (see Fig. 9)

$$|\Delta H_R| = 2.59 - 0.01\ E, r^2 = 0.55 \tag{3}$$

Both ΔH_R and the weighted activation energy are in kJ mol^{-1}. ΔH_R was calculated in accordance with the Appendix. Semenov [11] provided a similar relationship for the exothermic elimination and addition reactions of small atoms and small radical

$$|\Delta H_R| = 805.0 - 4E_f \tag{4}$$

where E_f represents the activation energy of the forward reaction. Equation (3) is not applicable for large values of ΔH_R or at $\Delta H_R = 0$. It was arrived at
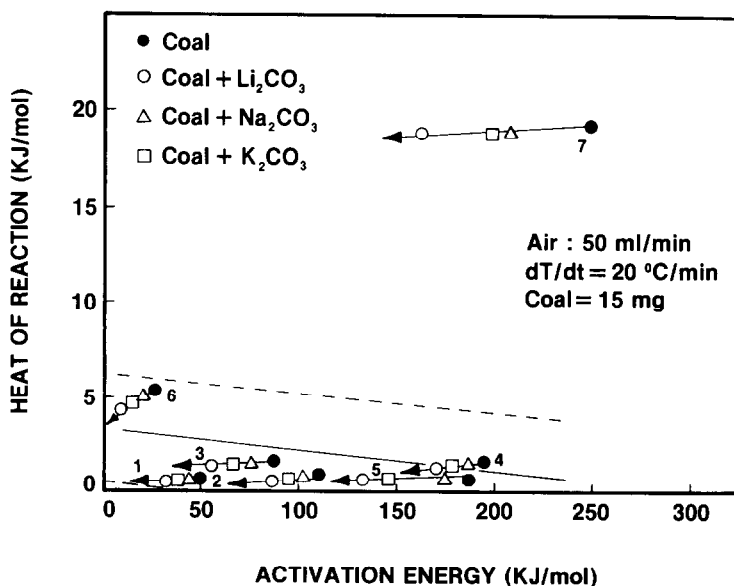

Fig. 9. Relationship between heat of reaction and activation energy in air (10^5 N m^{-2}).

by plotting values of E_f vs. $|\Delta H_R|$ for a large number of simple reactions with the exception of those involving electronegative radicals. A relationship between ΔH_R and E can also be determined for elementary reactions from kinetic and thermodynamic considerations [12,13]. Equations (1) and (2) may not, therefore, reflect the activity of an individual elementary reaction but indicates the average change occurring within a temperature interval, ΔT. The fact, however, that a relationship exists between the activation energy and the heat of reaction is significant for it indicates that (for the series of reactions occurring) the change in activation energy is determined by the change in heat of reaction [11].

The effect of changing the alkali metal in the salt, e.g., substituting K for Li, is shown in Table 4. The decrease in heat of reaction, ΔH_R, was also accompanied with a parallel decrease in activation energy ΔE correlated as follows

$$|\Delta H_R| = 0.06 + 0.06 \, \Delta E, \, r^2 = 0.89 \tag{5}$$

It is to be noted, however, that the constants in eqns. (1)–(5) are expected to differ according to the radicals involved [11].

EFFECT OF THE CATALYSTS ON CH_4, CO, AND CO_2 EMISSION

The catalysts reduced the amount of CH_4 evolved with Li_2CO_3 being most effective. This is possibly due to the inhibition of the reaction involving hydrogen transfer within the coal molecule and reactions which produce C–H and C–C bonds [14]. However, alkali metal salts increased the amount of CO and CO_2 during coal combustion in air. With Li_2CO_3, for example, the total CO and CO_2 emission increased by 15 and 5%, respectively. The presence of the catalysts brought forward the temperature at which the CO emission was maximum; by $\sim 20°C$ in the presence of Li_2CO_3. Maximum

TABLE 4

Effect of catalysts on heat of reaction and activation energy

Additive		523–618 K		618–723 K		723–823 K		823–938 K	
		E	$-\Delta H_R$	E	$-\Delta H_R$	E	$-\Delta H_R$	E	$-\Delta H_R$
Coal + Li_2CO_3	A	24.49	1.59	51.32	7.28	31.81	10.16	19.46	10.01
Coal + K_2CO_3	B	27.08	1.71	65.80	8.22	48.06	11.19	26.83	10.67
$B - A$		2.59	0.12	14.48	0.94	16.88	1.03	7.39	0.66

CO emission occurred at 683 K, when only coal was used. The change of CO/CO_2 mass ratio along the thermogram was also investigated. Below 703 K the CO/CO_2 ratio decreased exponentially with temperature. However, above 703 K the opposite effect occurred [15]. The general effect of the catalysts was to increase the CO/CO_2 ratio and the total amount of CO produced. McKee [1] provided a mechanism to explain the role played by the alkali metal salts in converting CO_2 into CO.

DISCUSSION

In a previous study on the same coal it was shown that the activation energy, preexponential factor, and order of reaction changed with operating parameters [3,15,16] which would suggest that the mechanism of reaction is changing and, therefore, the activation energy reported in this study is not an intrinsic value. What does it therefore represent? The results in this study show that the catalysts decreased both the activation energy and the heat of reaction. However, the reduction in activation energy was not always related to coal conversion (Fig. 10). A least squares fit of the data in Figs. 8 and 9 show that as ΔH_R increases the activation energy decreases which would indicate that the heat of reaction influences the chemical change typical of
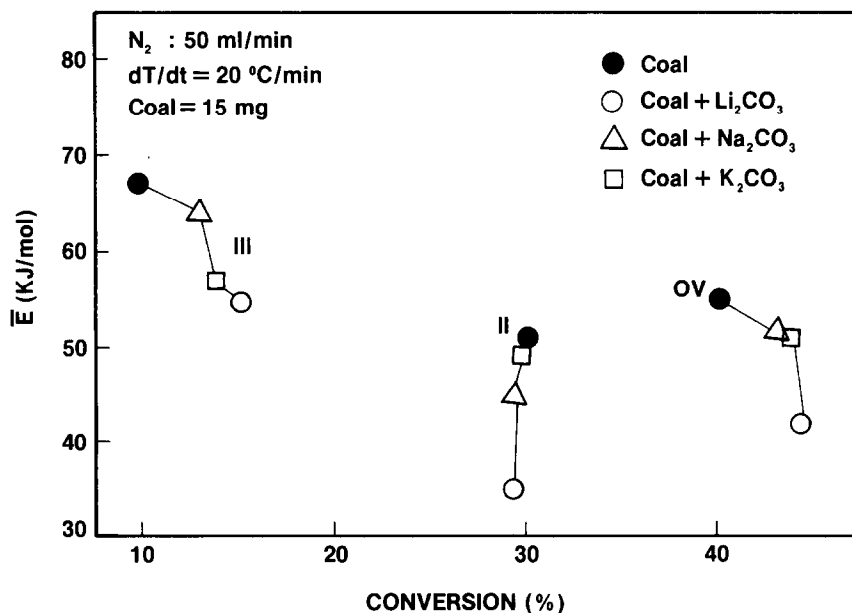

Fig. 10. Effect of catalysts on activation energy and conversion in different zones of the thermogram.

elementary reactions [13]. Such evidence reinforces the assumption that coal decomposition can be described as a first-order process [6].

The reduction in coal mass decomposed at low temperature in a nitrogen or carbon dioxide atmosphere may be attributed to the mobility of the catalyst layer since adsorption of a gas on a catalyst decreases the more mobile the catalyst [17]. At the higher temperature range (zone III) in a nitrogen or carbon dioxide atmosphere (Figs. 5 and 6) the catalysts increased the coal conversion resulting in a net increase in coal decomposed.

Finally, the fact that the alkali metal salts increased the amount of carbon monoxide produced, at such low temperatures, is important from a pollution viewpoint. It is, however, difficult to predict to what extent the amount of Na_2O and K_2O in coal ash will catalyze CO formation while exiting from a combustion system without considering, e.g., the temperature and residence time [18].

CONCLUSIONS

(1) Alkali metal salts increased (a) overall coal decomposition and (b) CO emission.

(2) Li_2CO_3 was the most effective in all atmospheres.

(3) Mixed catalysts are more effective than single catalysts.

(4) A relationship between heat of reaction and activation energy exists.

(5) The decrease in activation energy did not always reflect an increase in coal reactivity.

NOMENCLATURE

A	pre-exponential factor in the Arrhenius equation
A_p	peak area (cm^2)
C	conversion (dimensionless)
dC/dt	rate of conversion (min^{-1})
E	activation energy (kJ mol^{-1})
$\bar{E}_{II}$	a weighted average E corresponding to decomposition zone II (kJ mol^{-1})
$\bar{E}_{III}$	a weighted average E corresponding to decomposition zone III (kJ mol^{-1})
$\bar{E}_{ov}$	a weighted overall E based on $\bar{E}_{II}$ and $\bar{E}_{III}$ (kJ mol^{-1})
E_f	activation energy of an elementary reaction in the forward direction (kJ mol^{-1})
ΔH_R	the heat of reaction (kJ mol^{-1})
k	rate constant in Arrhenius equation (min^{-1})
K_c	the calibration coefficient in DTA (J min^{-1} °C)

m mass at T (mg)
m_i mass at T_i (mg)
m_f mass at T_f (mg)
dm/dt rate of mass loss (mg min^{-1})
n order of reaction (dimensionless)
r^2 the correlation coefficient
R ideal gas constant (8.31 J mol^{-1} K)
s chart speed (cm min^{-1})
T temperature (K)
ΔT_s differential temperature sensitivity (°C min^{-1})
dT/dt heating rate (°C min^{-1})
t time (min)
Δ difference

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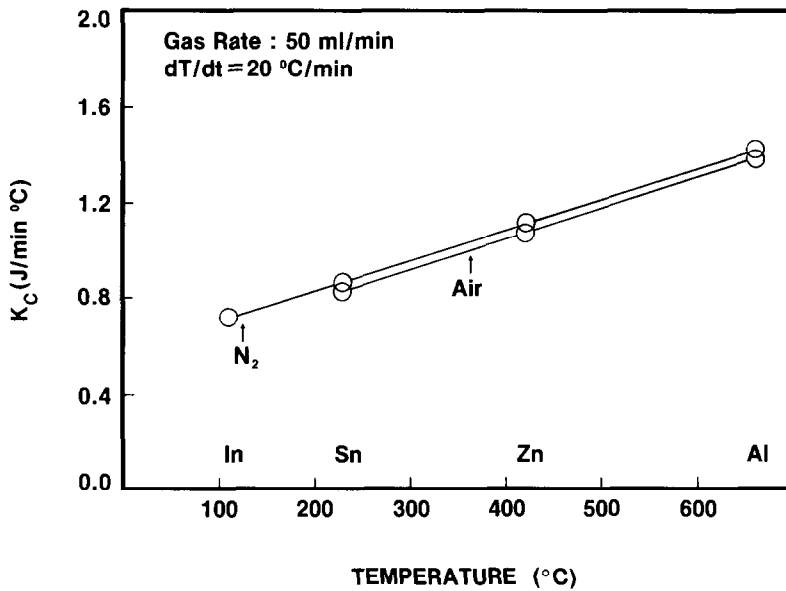Fig. 11. 1200°C DTA cell heat flow calibration curves in air and nitrogen (10^5 N m^{-2}).

APPENDIX

Calculation of ΔH using DTA

The heat of reaction using DTA was determined from the peak area and using the following equation [5]

$$\Delta H_R = \frac{K_c A_p \Delta T_s}{ms} 10^{-3}$$

(1A)

The values of K_c were determined from Fig. 11. ΔH_R calculated from eqn. (1A) is in kJ g^{-1}. It was converted to kJ mol^{-1} from a knowledge of the change of coal composition along a thermogram.