

EFFECT OF CALCIUM CHLORIDE AND CALCIUM ACETATE ON THE REACTIVITY OF A LIGNITE COAL AT LOW HEATING RATE

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ABSTRACT

The effect of calcium chloride and calcium acetate on the rate of decomposition of a lignite coal and its char was investigated under both pyrolysis and combustion conditions. The experiments were undertaken in a thermogravimetric analyzer under low ($20^{\circ}\text{C min}^{-1}$) and intermediate ($2100^{\circ}\text{C min}^{-1}$) heating rates.

Both calcium chloride and calcium acetate slightly reduced the amount of coal decomposed at 10^5 N m^{-2} in a nitrogen atmosphere. However, the inhibiting effect of calcium acetate was dependent on the sample size and packing density. In the presence of oxygen, addition of calcium chloride to coal produced two opposite effects: at low temperatures an inhibiting effect due to the chloride and at higher temperatures a promoting effect due to the catalytic role of the calcium. Lastly, the additives reduced the apparent activation energy and increased the heat reaction of the lignite coal.

NOMENCLATURE

A	pre-exponential factor in the Arrhenius equation
E	activation energy (kJ mol^{-1})
\bar{E}_{ov}	a weighted overall E based on eqn. (2) (kJ mol^{-1})
k	rate constant in the Arrhenius equation (min^{-1})
m	mass at T (mg)
m_i	initial mass (mg)
m_f	final mass (mg)
dm/dt	rate of mass loss (mg min^{-1})
n	order of reaction taken as unity
R	the gas law constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R_{max}	maximum reactivity (min^{-1})
T	absolute temperature (K)

T_{\max}	absolute temperature at R_{\max}
$T_{0.4}$	absolute temperature at the 40% decomposition point (K)
ΔH	heat of reaction (kJ g^{-1})

INTRODUCTION

The purpose of this work was to compare the effect of calcium chloride and calcium acetate on the reactivity of coal. The experiments were performed in a thermogravimetric analyzer (TGA) using the temperature programming mode (i.e., non isothermal). Because of the possible overlapping of the devolatilization and char combustion stage, the effect of the additives on char produced from treated and untreated coal was also investigated. The temperature programming mode has frequently been used to understand the characteristics of coal pyrolysis and combustion because fewer experiments are required to cover the whole temperature range of decomposition [1–3]. Because of the complex nature of coal, determining activation parameters using non isothermal methods poses a problem, since the mechanism for coal decomposition is still not understood. As a result the activation parameters obtained in this way are subject to the operating conditions and methods used in their determination [1,2]. However, the Arrhenius equation with first order reaction rate was recommended [3–6]. In this case the procedure activation energy may be considered to be proportional to the net heat of reaction occurring in the temperature interval for which the activation energy is valid [4,5].

EXPERIMENTAL

Coal and char preparation [7]

Lignite coal from Velva Mine, North Dakota was used. The proximate analysis (as received) of the material indicated 33.9% moisture, 32.9% volatiles, 27.5% fixed carbon and 5.7% ash. The coal particle size was $-100, +270$ mesh.

The coal was treated with a 0.13 M solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ [$0.75 \text{ ml (mg of coal)}^{-1}$] to produce the desired loading of 1.40% CaCl_2 by weight on a dry basis. The untreated coal was impregnated with water and dried, following the same procedure used for the additive treated coal. Calcium acetate was added [same calcium bases: $1 \times 10^{-4} \text{ gm atm (gm of coal)}^{-1}$].

Coal-char was prepared at 1248 K by pyrolyzing coal (both treated and untreated) in a constant stream of nitrogen (25.5 ml min^{-1} at S.T.P.).

TGA procedure

About 10 mg of coal was decomposed in a Du Pont 951 thermogravimetric analyzer connected to a Du Pont 990 thermal analyzer. The samples were heated at $20^{\circ}\text{C min}^{-1}$ from room temperature to a maximum temperature of 1173 K. The flow of nitrogen and of air was fixed at 300 ml min^{-1} , measured at room temperature ($\sim 293\text{ K}$).

The conditions for the isothermal runs were somewhat different. About 2 mg of coal was spread evenly on the platinum pan. The sample was introduced into the furnace after about 300 s from the time the set temperature of 1173 K was reached. The sample heating rate at this temperature was about $2100^{\circ}\text{C min}^{-1}$, which can be classified as an intermediate rate of heating compared to the slower rate produced in the programming mode. The oxygen and nitrogen gases were provided by the Matheson Company and were both of high purity.

DSC procedure

A Du Point 910 differential scanning calorimeter (DSC) connected to a Du Pont 990 controller was used to measure the heat of reaction of the coal samples. About 10 mg of coal was placed in an alumina pan and heated at a constant rate of $20^{\circ}\text{C min}^{-1}$. The gas flow rate was kept at 300 ml min^{-1} for both the pyrolysis and combustion runs. Coal char was used as reference material during the pyrolysis runs whereas ash was used during the combustion runs.

THEORY

The experimental activation energy was calculated using the following widely used equation, assuming $n = 1$ [2,3,5]

$$\frac{-dm/dt}{m_i - m_f} = A \exp(-E/RT) \frac{m - m_f}{m_i - m_f} \quad (1)$$

where m_i and m_f refer to the initial and final mass; dm/dt , the mass-loss rate; A , pre-exponential factor; E , the apparent activation energy; T , absolute temperature; and R , the gas constant.

An overall activation energy was then calculated as follows [1,3]:

$$\bar{E}_{\text{ov}} = \sum_{i=1}^n E_i X_i = E_1 X_1 + E_2 X_2 + \dots + E_n X_n \quad (2)$$

where X_i , in this case, is the mass fraction, and E_i the activation energy corresponding to a temperature interval i along the TG curve. The maximum rate of mass-loss $(dm/dt)_{\text{max}}$ is often used as a measure of coal

reactivity under a given set of condition [2]. However, the following representation [8] is more useful as it takes into account the effect of sample mass

$$R_{\max} = \frac{1}{m_i} \left(\frac{dm}{dt} \right)_{\max} \quad (3)$$

RESULTS

Decomposition under a nitrogen atmosphere

A typical thermogravimetric heating curve for coal in nitrogen is shown in Fig. 1. The zone labeled I, around 373 K, was due to loss of inherent moisture, and the major decomposition zone labeled II, at about 731 K, was due to the volatiles released. Further decomposition occurred at a relatively constant mass-loss rate until the final set temperature of 1173 K was reached. Table 1 shows the effect of calcium chloride and calcium acetate on a number of parameters related to zone II: T_{\max} , the temperature at which the maximum rate of mass-loss occurred; R_{\max} , the reactivity at T_{\max} (m_i) $_{\max}$; $t_{0.4}$, the time at which 40% (dry and free) of the sample had decomposed; and $T_{0.4}$, the temperature at $t_{0.4}$. T_{\max} (II) did not vary with the amount of calcium chloride added, not did R_{\max} vary significantly. However, from Fig. 1 it is clear that the presence of additional chloride reduced the volatile matter evolved at these low heating rates ($20^\circ\text{C min}^{-1}$). The cumulative yield of volatile material produced in each case is summarized in Table 2.

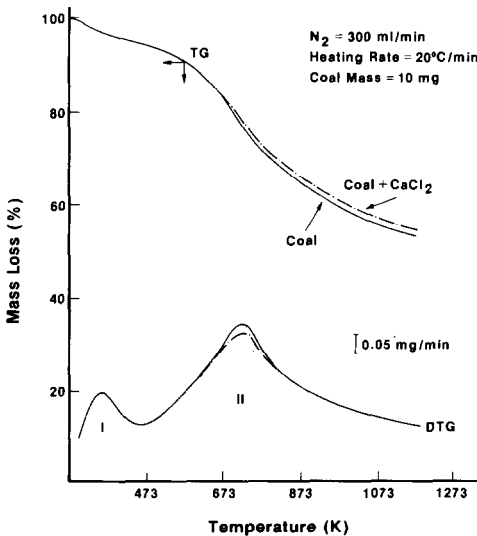


Fig. 1. Effect of CaCl_2 on the decomposition of coal in nitrogen (10^5 N m^{-2}).

TABLE 1

Effect of additives on the TG and DTG decomposition parameters produced during slow pyrolysis of coal in nitrogen ($20^{\circ}\text{C min}^{-1}$)

Sample	T_{\max} (K)	R_{\max} (min^{-1})	$t_{0.4}^a$ (s)	$T_{0.4}^a$ (K)
Coal	713 ± 5	0.0365	1815	630 ± 5
Coal + CaCl_2	713 ± 5	0.0358	2055	710 ± 5
Coal + $\text{Ca}(\text{CH}_3\text{COO})_2$	713 ± 5	0.0366	1830	635 ± 5

^a Dry ash free basis (daf).

TABLE 2

Effect of additives on the cumulative yield of volatile material evolved during slow pyrolysis of coal in nitrogen ($20^{\circ}\text{C min}^{-1}$)

Sample	Yield (%) (daf)	Normalized mass fraction ^a
Coal	47.2 ± 0.7	0.866
Coal + CaCl_2	45.2 ± 0.5	0.829
Coal + $\text{Ca}(\text{CH}_2\text{COO})_2$	47.0 ± 0.6	0.862

^a Normalized with respect to the volatile matter in the parent coal (V.M. = 54.5%, daf).

TABLE 3

Effect of additives on the cumulative yield ^a of volatile material produced during pyrolysis of coal in nitrogen. Furnace set at $T_{\text{iso}} = 1173\text{ K}$ ($\sim 2100^{\circ}\text{C min}^{-1}$)

Sample	Yield (%) (daf)	Normalized mass fraction ^b
Coal	51.2 ± 0.2	0.939
Coal + CaCl_2	47.8 ± 0.4	0.877
Coal + $\text{Ca}(\text{CH}_3\text{COO})_2$	49.1 ± 0.2	0.901

^a The cumulative yields of volatile within 60 s.

^b Normalized with respect to the volatile matter in the parent coal (V.M. = 54.5%, daf).

Table 3 shows the mass-loss results obtained when the furnace temperature was set a 1173 K, which provided an average sample heating rate of $\sim 2100^{\circ}\text{C min}^{-1}$. In this case the overall sample decomposition rate was decreased in the presence of either calcium acetate or calcium chloride. However, the effect of calcium acetate was somewhat less than that of calcium chloride.

Decomposition in air

The effect of the additives on the rate of mass-loss in air is shown in Fig. 2. Following the evolution of moisture (zone I) a second zone (II) occurred

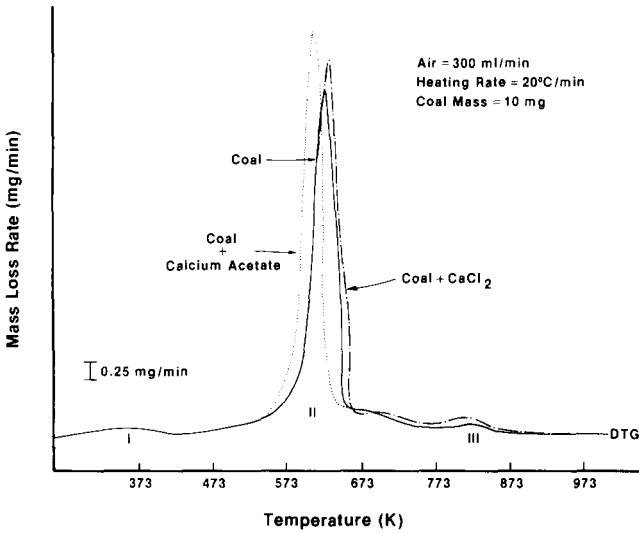


Fig. 2. Effect of additives on the decomposition of coal in air (10^5 N m^{-2}).

which represented overlapping reactions such as oxidative devolatilization and combustion [8].

It is clear from Fig. 2 that calcium acetate promoted coal decomposition whereas calcium chloride produced the opposite effect. However, both additives increased coal reactivity [i.e., $(dm/dt)_{\max}/m_i$] in both zone II and zone III. This was not true under pyrolysis conditions (see Fig. 1).

Beyond 973 K the curves tended to flatten. The higher residue in Fig. 2 at the final temperature (1173 K) may partly be attributed to reactive sulfur retained in the coal in the form of calcium sulfate [7,9,10]. This may also partly explain the higher final mass of residue (m_f) in Table 4.

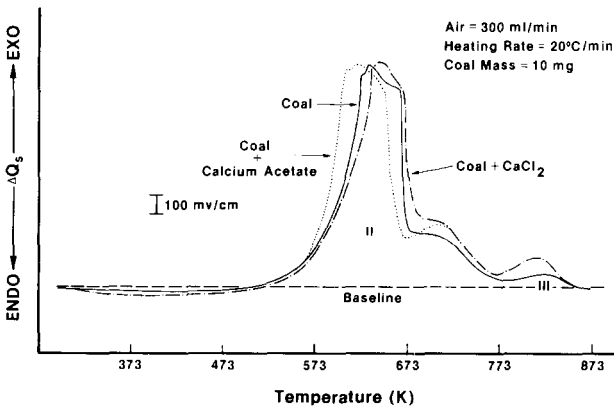


Fig. 3. DSC heating curves for coal in air (10^5 N m^{-2}).

TABLE 4

Decomposition parameters for coal combusted in air at $20^{\circ}\text{C min}^{-1}$

Sample	T_{\max} (II) (K)	T_{\max} (III) (K)	ΔH (kJ g^{-1})	m_f (%)	\bar{E}_{ov} (kJ mol^{-1})
Coal	615	805.5	21 ± 2	8.6 ± 0.2	127 ± 5
Coal + CaCl_2	620	795.5	28 ± 3	9.8 ± 0.3	93 ± 5
Coal + $\text{Ca}(\text{CH}_3\text{COO})_2$	595	795.0	34 ± 2	9.7 ± 0.2	78 ± 5

DSC runs in air

Figure 3 shows a number of DSC heating curves for coal. The results obtained when coal was reacted in air agree with those obtained using the TGA, namely calcium acetate shifted zone II to a lower temperature whereas calcium chloride produced a shift to higher temperatures. The DSC curves, however, illustrated more clearly the promoting effect of both additives in zone III and provided somewhat greater details in the temperature interval 673–773 K, showing the presence of another reaction zone.

Combustion of char in air (Fig. 4) was also enhanced as a result of treating the parent coal with calcium chloride. Only one exothermic zone was clearly formed (Fig. 5). The char was believed to be mostly fixed carbon.

Activation energy and heat of reaction

It is clear from Table 4 that both calcium chloride and calcium acetate reduced the overall activation energy of coal and increased the overall heat

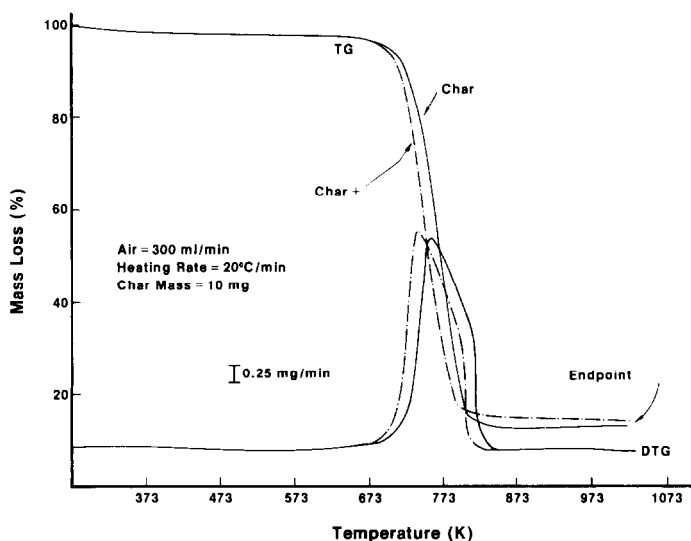


Fig. 4. Effect of CaCl_2 on the decomposition of char in air (10^5 N m^{-2}). Char + means from CaCl_2 treated coal.

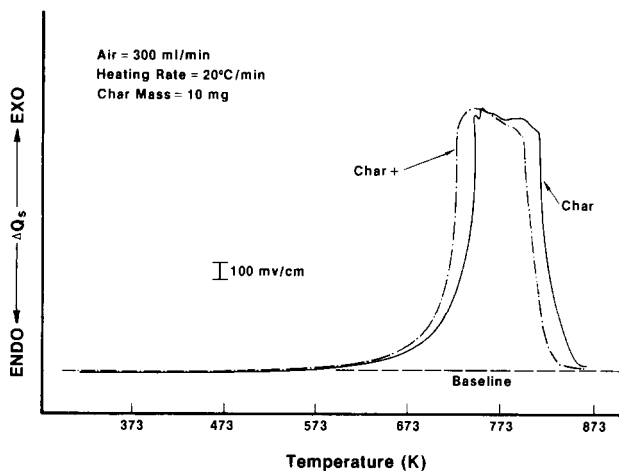


Fig. 5. DSC heating curves for char in air (10^5 N m^{-1}). Char+ means from CaCl_2 treated coal.

TABLE 5

Decomposition parameters for char combusted in air at $20^\circ \text{C min}^{-1}$

Sample	T_{max} (K)	m_f	ΔH (kJ g^{-1})	\bar{E}_{ov} (kJ mol^{-1})
Char	745	13.5 ± 0.2	29 ± 3	165 ± 5
Char from CaCl_2 treated coal	728	14.4 ± 0.3	39 ± 3	150 ± 4

of reaction. Although the effect was less pronounced in the case of char (Table 5), the trend was still true. It is this relationship between E and ΔH for coal, observed in an earlier study [5,10], that prompted us to suggest that this apparent activation energy is a measure of the net heat resulting from a number of reactions within a given temperature interval.

DISCUSSION

Under slow pyrolysis conditions ($20^\circ \text{C min}^{-1}$), the reduction in mass-loss occurred only when calcium chloride was added to coal and not when calcium acetate was the additive. However, at higher heating rates ($2100^\circ \text{C min}^{-1}$) calcium acetate also produced an inhibiting effect. The inhibiting effect of the chloride ion is attributed to its ability to form cross-links with coal [11,12] and to promote condensation and molecular growth reactions as opposed to degradation reactions [14]. The cross-links formed during the early stages of decomposition will reduce the degree of graphitization of the resultant char making it burn more easily [7,13], whereas the inhibition produced (at the higher heating rate) by calcium acetate may be attributed

to the formation of calcium compounds (e.g. CaCO_3 , CaO) which promote cracking and polymerization of tar molecules before volatilization occurred. Previous workers [15] showed that when a bituminous coal pretreated with calcium oxide was rapidly pyrolyzed ($1000^\circ\text{C s}^{-1}$), its tar yield and yield of light hydrocarbons (e.g., methane) were reduced. Another study [5] involving a subbituminous coal pretreated with alkali carbonates showed that an inhibiting effect occurred first at a low temperature, followed by a promoting effect at higher temperatures. The latter effect occurred at $\sim 938\text{ K}$ in the case of lithium carbonate. The coal was combusted in air at $20^\circ\text{C min}^{-1}$.

The different results obtained during pyrolysis when calcium acetate was added to coal were mainly attributed to the different sample masses used, i.e., 2.40 mg in the intermediate heating rate experiments and 10 mg in the slow heating rate experiments. Increasing the sample mass or the system pressure (see, e.g., ref. 16) has the effect of delaying the release of volatile material in the coal, promoting secondary char-forming reactions [17] which explains why addition of calcium acetate did not significantly change the mass-loss rate during pyrolysis. However, when the sample can be spread thinly on a sample pan, as was possible with the 2.40 mg sample, char-forming reactions are less likely to occur [17] and the inhibiting effect of additives becomes apparent.

During combustion of calcium chloride treated coal, two opposing effects may occur: in the early decomposition stage the inhibiting effect of the chloride is more important. Halogen acids or other chlorinated hydrocarbons will react with H via such low energy reaction steps [18]



causing the inhibition of important chain branching steps. This explains why the reaction in zone II (Fig. 3) was delayed until the temperature was high enough for the oxidizing reactions to become important. The calcium in the form of its oxide may promote the extent of decomposition via, e.g., [19]



When conditions favor deactivation as a result of three body collisions, the promoting, i.e., catalytic, effect of metal salts observed at temperature less than 1200 K may not be very important. Such conditions may exist at higher temperatures ($\sim 1700\text{ K}$) typical of coal flames [20].

CONCLUSIONS

1. Addition of calcium chloride or calcium acetate to a lignite coal slightly reduced the amount of material decomposed at 10^5 N m^{-2} in N_2 .

2. The extent to which calcium acetate inhibited coal decomposition in nitrogen was dependent on the sample mass and packing density.
3. In an oxidizing environment addition of calcium chloride to coal retarded its decomposition at first, due to the effect of the chloride. It then promoted coal decomposition at higher temperatures where the catalytic effect of the calcium was dominant.
4. The decrease in apparent activation energy was accompanied by an increase in heat of reaction. This was true for both coal and its char.

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