

Review

A review of the derivative thermogravimetric technique (burning profile) for fuel combustion studies

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Abstract

Burning profiles obtained by derivative thermogravimetric analysis are useful for obtaining relative combustion characteristics of fuels and for predicting combustion performance in boilers. However, the interpretation of these profiles is not always straightforward, particularly with respect to the combustion peaks. In this paper, the use of burning profiles for coal reactivity studies is reviewed. Factors which affect the appearance of the combustion peaks in the burning profiles and complicate data interpretation are summarized. Special emphasis is given to catalytic effects, because this factor is often not adequately considered when interpreting the data.

INTRODUCTION

Burning profiles give detailed information about a fuel from the onset of oxidation to complete burnout [1] and are useful for predicting relative combustion characteristics. The technique is particularly useful for evaluating unusual fuels in which sample quantities are insufficient for full-scale burning tests [2]. Because coals with similar burning profiles would be expected to behave similarly during combustion, burning profiles are often used to predict combustion behavior of coal in large boilers. By comparing the burning profile of an unknown coal with those from coals with known performance characteristics, predictions can be made regarding the proper furnace size and design, the type and arrangement of burners, residence time, excess air, and auxiliary fuel requirements [2, 3]. In this paper, the thermoanalytical technique used to obtain burning profiles of coals is reviewed and interpretation of the profiles is discussed.

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Factors which affect the appearance of the combustion peaks in the burning profiles and complicate data interpretation are summarized.

DESCRIPTION OF METHOD

To obtain a burning profile, a sample of coal is heated at a constant rate to 700–900°C in air in a thermogravimetric analyzer (TGA). The sample weight (or, alternately, the percent of the original sample weight) is measured and plotted as a function of either heating time or temperature. This plot is known as a TGA curve. A derivative thermogravimetric (DTG) curve, or burning profile, is obtained by plotting the first derivative of the TGA data, thereby depicting the rate of weight loss as a function of temperature. Examples of TGA and DTG curves for a raw Illinois No. 6 coal are shown in Fig. 1. However, it must be emphasized that burning profiles can vary considerably and that the DTG curve shape and peak positions shown in Fig. 1 are not necessarily representative of other coals.

In order to make comparisons between different samples, factors such as sample quantity, heating rate, and air flow rate should be the same between tests. Conditions vary widely among studies and include heating rates of 5–15°C min⁻¹, samples sizes of 5–300 mg, and air flow rates of 50–800 cc min⁻¹. Of these, the air flow rate has the least effect on burning profiles. Proper selection of test conditions will depend on instrumental limitations and the nature of the samples. Unless otherwise noted, all

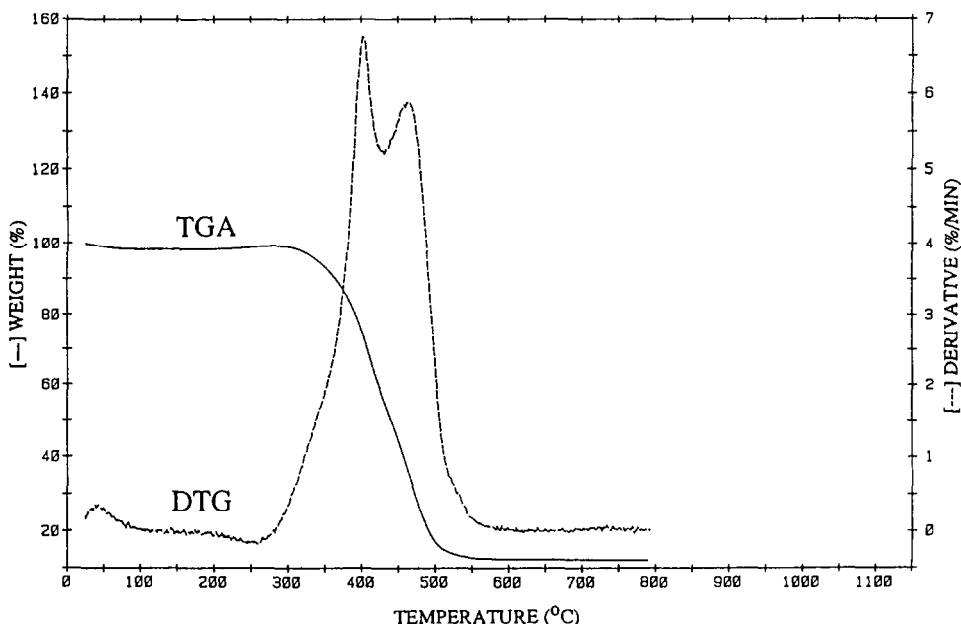


Fig. 1. TGA and DTG (burning profile) curves obtained for an Illinois No. 6 coal.

burning profiles shown in this paper were obtained using 10 mg samples, a heating rate of $100^{\circ}\text{C min}^{-1}$, and an air flow rate of 75 cc min^{-1} .

DISCUSSION

Features of the burning profile

As sample temperature increases, a number of different events are observed. A classic burning profile showing those events is presented in Fig. 2. If there is moisture in the sample, a peak will occur typically at about 100°C or below. After moisture loss, the curve sometimes has a negative deflection (weight gain) because of oxidation of the organic matter [4]. This appears as a downward trend rather than a peak. When the curve rises above the “zero line”, weight loss from the expulsion of volatile matter has begun. This point is known as the “volatile matter initiation temperature” (IT_{vm}) [4, 5]. With further temperature increases, the rate of weight loss continues to rise as the volatile release accelerates. At the point where the slope suddenly increases prior to the peak maximum, the rate of weight loss accelerates due to the onset of combustion [4, 5]. This inflection point is called the “fixed carbon initiation temperature” (IT_{fc}) [4]. Although devolatilization is not completely separated from char burning, much of the volatile matter has been

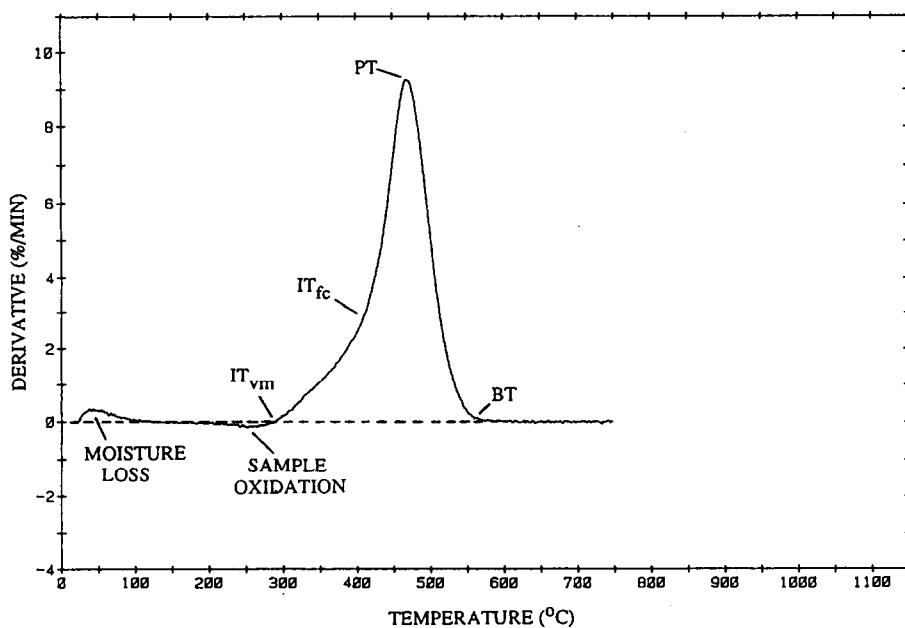


Fig. 2. Simple burning profile showing moisture loss, sample oxidation, volatile matter initiation temperature (IT_{vm}), fixed carbon initiation temperature (IT_{fc}), peak temperature (PT), and burnout temperature (BT).

released at this point, and combustion is the major weight loss mechanism taking place.

The location of the primary peak (or peaks) is the temperature at which the maximum combustion rate occurs. Devolatilization is essentially complete at this point [6]. This peak temperature (PT) reflects relative reactivities of the fuels and is generally considered to be the most important feature of the DTG curve. Under the proper conditions, the PT should be repeatable to within about 5°C. Coals with lower peak temperatures are indicative of more reactive fuels and can generally be ignited and burned more easily. Such coals would be expected to burn more completely in the lower part of a boiler furnace, while coals exhibiting high peak temperatures burn relatively slowly and would require longer residence times or higher temperatures for complete combustion [2]. The peak height is proportional to burning intensity and the area under the peak is approximately proportional to the total heat liberated [2]. The height of the DTG peak is related to reactivity based on the equation

$$R = 1/W_i(dw/dt)_{\max}$$

where R is the reactivity, W_i the initial weight of dry, ash-free (DAF) coal (mg), and dw/dt_{\max} the maximum rate of weight loss (mg min^{-1}) [7]. Thus, DTG peak heights will indicate relative reactivities of the coals if the DAF weights are equal. The major factors controlling the reactivity of carbonaceous solids to oxygen are the concentration of active sites, diffusion limitations on how rapidly the oxygen can reach those sites, the presence of catalytic inorganic impurities, and the degree of oxidation of the sample [7, 8].

The “burnout temperature” (BT) is the temperature at which the rate of weight loss returns to zero, or by some definitions, where the rate of weight loss becomes less than 1% per minute [6]. This temperature can also have important combustion implications relating to residence time and furnace temperature.

Some researchers have normalized burning profiles from different coals by taking into account the volatile matter and fixed carbon contents [7]. In doing so, the sample weights necessary to provide the same amount of reactive matter in each sample were calculated and peak heights could be directly compared. Based on the analysis of numerous coals, the peak temperature of combustion tended to decrease as the VM/FC ratio decreased. For a given VM/FC ratio, the peak temperature varied by as much as 50°C among coals, and deviations of 20°C were common. Results also indicated that low-rank coals react at lower temperatures and show a higher rate of combustion than higher rank coals. Increased reactivity for lower rank coals has also been observed by other researchers [9]. Some low-rank coals, such as lignites, can have two or more major burning

peaks. This has been termed “false ignition” because it implies that the coal is ignitable at a relatively low temperature, even though it may not burn completely until higher temperatures are reached [4].

Factors affecting combustion peaks

As noted earlier, experimental factors such as sample size and heating rate affect the burning profiles and should be consistent from test to test. Those factors can affect the shape of the DTG curve as well as the peak locations. The combustion peaks in a burning profile are of particular interest. Some coals exhibit only a single peak, while others exhibit multiple peaks.

Sample ignition (burning with flame) is one particular problem which can not only result in multiple combustion peaks, but can also invalidate the test for many applications. The chance of this occurring increases with increases in sample size or heating rate. Because sample ignition, or thermal runaway, is uncontrolled and non-repeatable [6], it is preferable to obtain burning profiles without sample ignition. If ignition does occur, multiple combustion peaks will usually result as the sample flares up and dies down in an unpredictable manner. This effect is shown in Fig. 3. For that burning profile, a 20 mg sample of coal was used with a heating rate of $10^{\circ}\text{C min}^{-1}$.

In cases where the sample thermocouple is above the sample, ignition

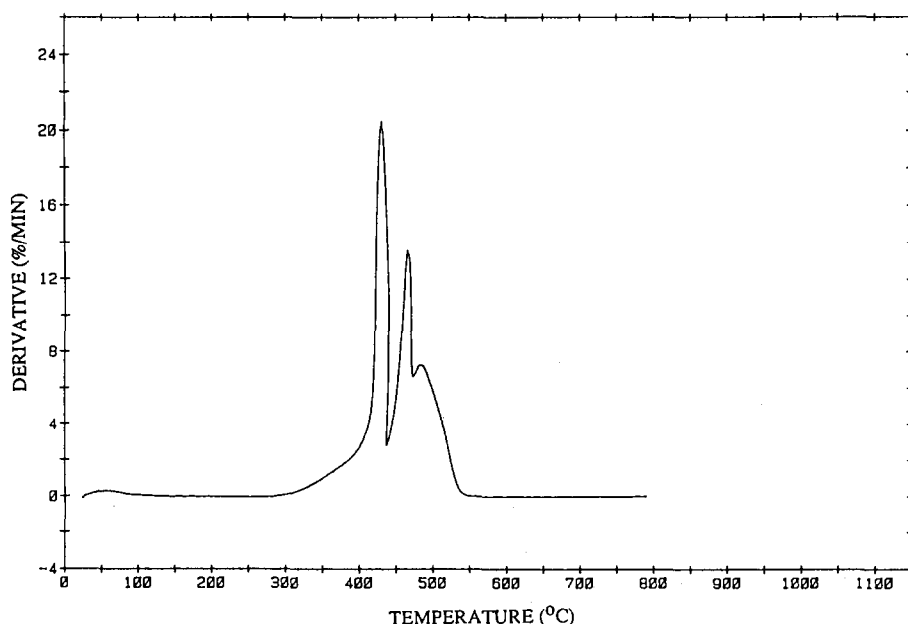


Fig. 3. Burning profile with multiple combustion peaks due to sample ignition.

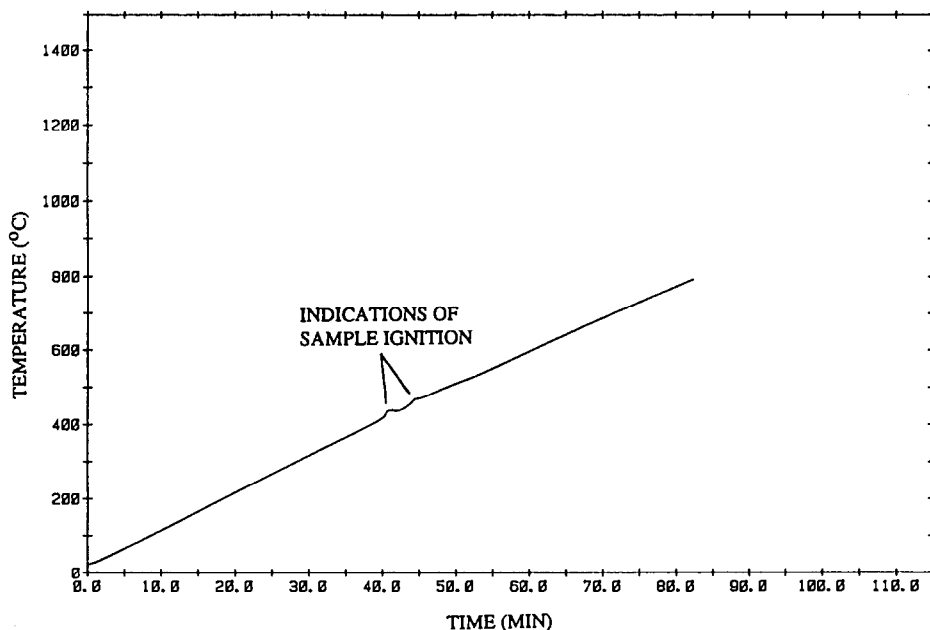


Fig. 4. Sample temperature profile (corresponding to burning profile shown in Fig. 3) showing deviations from the linear heating rate.

can be detected by plotting sample temperature against time. Sample ignition is likely if there are small positive deviations from the linear heating rate. This is shown by the sample temperature profile in Fig. 4, which corresponds to the burning profile shown in Fig. 3. The test should be considered suspect if the sample exhibits an erratic burning profile, such as the one shown in Fig. 3, as well as aberrations in the temperature profile. When the test was rerun using 10 mg of sample (rather than 20 mg), no deviations from the linear heating rate were observed and the burning profile was identical in shape to the one shown in Fig. 2.

In the absence of sample ignition, explanations which have been offered as the reason for multiple (usually bimodal) combustion peaks include particle size effects, reduced accessibility to oxygen from swelling of the coal, combustion of aliphatic versus aromatic coal fractions, catalytic effects, and combustion of different maceral fractions. However, the explanations are frequently speculative and are often not verified. Single explanations for multiple combustion peaks are sometimes postulated without experimental support or without considering other possibilities.

Particle size effects can alter the shape of the burning profile dramatically. In one study, a coal sample that was plus 125 microns showed a bimodal combustion peak, but showed only a single broad peak when ground to minus 75 microns [6]. It was reported that particle size effects can be minimized by grinding coals to minus 75 microns using a procedure

which gives reproducible size distributions. In the same study, considerable maceral effects were observed, with PT and BT being significantly lower for vitrinite than for inertinite. The PT and BT of both macerals tended to increase with increasing rank, although differences in reactivity between vitrinite and inertinite diminished with increasing rank.

In other work on maceral effects, demineralized samples of vitrinite, inertinite, and liptinite macerals had significantly different PTs and also exhibited different burning intensities [9]. It was also noted that variations in reactivity due to differences in coal rank were of the same order of magnitude as variations due to different macerals within a sample. Differences in PT between the macerals studied generally did not differ by more than 20°C.

Catalytic effects can also cause bimodal combustion peaks, although this variable is often overlooked. The degree of catalytic effect depends on the amount, type, chemical form, e.g. sulfate versus oxide, and degree of dispersion of mineral species [8,10]. The catalytic effects of inorganic impurities on carbon gasification are well known. In one summary of work in that area, it was noted that results varied substantially from study to study with respect to the effectiveness of various catalysts [11]. However, experimental procedures and parameters were also different.

Numerous studies on catalytic effects on the reactivity of coal chars in air have been performed. In one study, the effects of mineral matter on the reactivity of chars from fresh and weathered coals were studied by leaching the coals with HCl prior to charring. The weathered samples were more reactive than the fresh samples. Acid washing the raw coals increased the reactivity of chars from the fresh coals, but decreased reactivity of chars from the weathered coals [10]. For some coals, ion-exchangeable calcium was considered to be the predominant catalytic species. For other coals, it was speculated that iron may be largely responsible for the catalytic effects. The degree of catalytic activity of iron was believed to be a function of the ratio of ferrous to ferric iron (the higher the better) and how rapidly the ferrous iron oxidizes to the ferric state.

In another study, removing mineral matter from low-rank coals prior to charring generally decreased char reactivity, while the opposite tended to be true for higher rank coals [8]. In a third study, chars from 21 U.S. coals of varying ranks were the most reactive if they contained high amounts of Mg and Ca impurities, while no correlation was found for K, Na, and Fe. The reactivity of chars from some of the coals was significantly affected by leaching the raw coals with either HCl only or with HCl followed by leaching with HF prior to making the chars [12]. Other researchers found that CaO and CaCO₃ exhibited significant catalytic activity during the gasification of a lignite char and a synthetic char in 10% oxygen (90% nitrogen) [13].

In related work, coal combustion exotherms (obtained by differential thermal analysis) were shifted to much higher temperatures after acid washing the coal [14]. Peak shifts after acid washing were believed to be a result of the extraction of metal ions by the acid.

Studies on catalytic effects performed at Ames Laboratory

To demonstrate the importance of catalytic effects, a series of tests were performed at Ames Laboratory using an Illinois No. 6 coal. The burning profile for the raw coal had a double combustion peak. The possibility of this being attributable to particle size effects was examined by obtaining burning profiles on separate aliquots of coal ground to minus 60 (250 μm), 200 (74 μm), and 325 (44 μm) mesh. Because the burning profiles were nearly identical for each mesh size, particle size effects do not appear to be the cause of the double combustion peak.

When the raw coal was washed with hot (60°C) 10% HCl, followed by a hot water wash, the coal exhibited only a single combustion peak, as shown in Fig. 5. In Fig. 5, it is also interesting to note that the two samples exhibited nearly identical BTs but had different reactivities based on the shape and location of the combustion peaks. Although some researchers have used burnout temperatures as a measure of relative reactivities, these

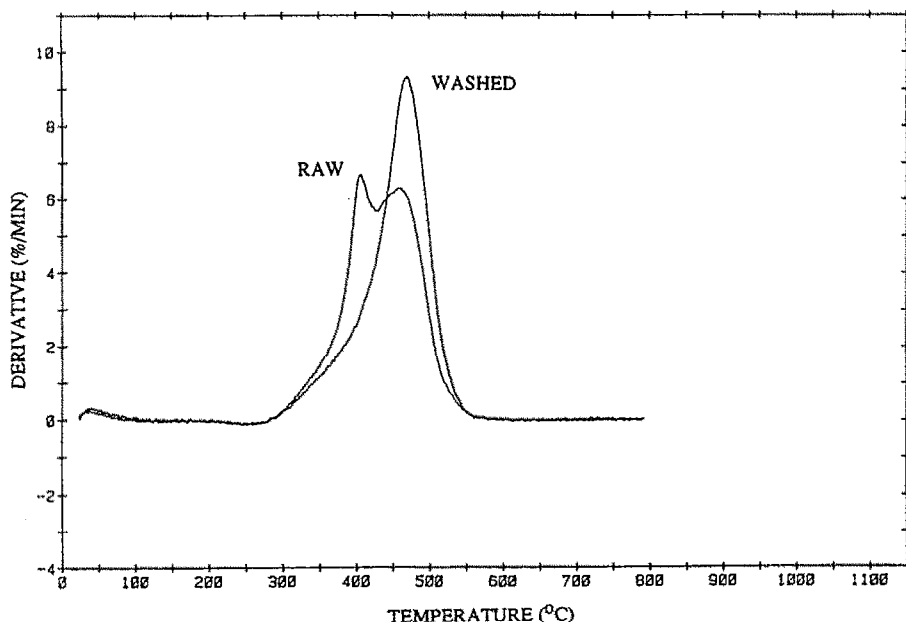


Fig. 5. Burning profiles for Illinois No. 6 coal before and after washing with 10% HCl and water.

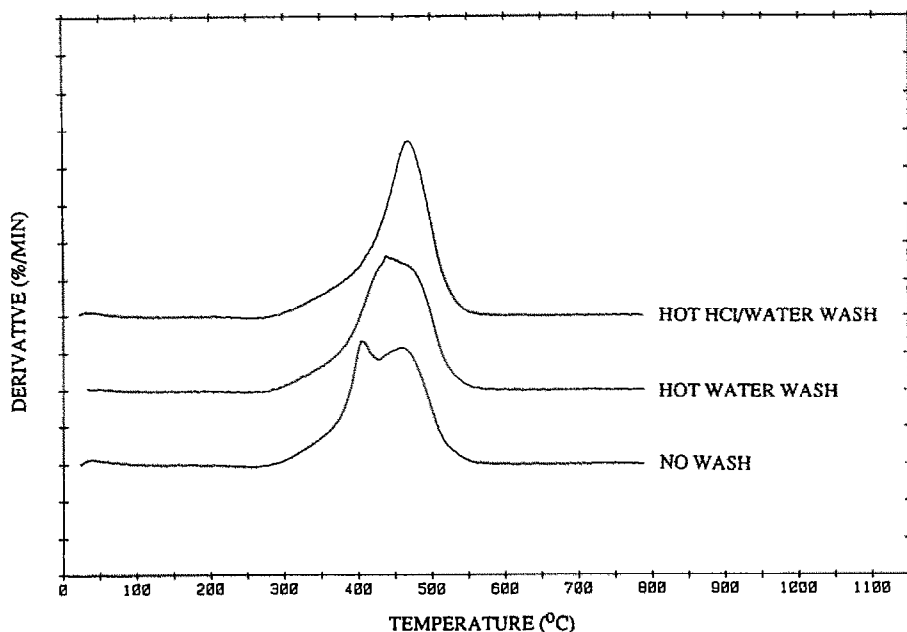


Fig. 6. Burning profiles for Illinois No. 6 coal before and after washing with hot water only and with hot 10% HCl followed by water washing. Profiles are offset vertically for clarity.

data indicate that it may be useful to use PTs as well as BTs when assessing coal reactivity.

When an aliquot of the raw coal was washed with hot water only, a burning profile intermediate between that of the raw coal and acid-washed coal was obtained. These profiles are shown in Fig. 6. These data suggest that the double peak in the burning profile for the raw coal is not due to maceral effects or to the combustion of aliphatic versus aromatic portions of the coal. If those factors were affecting the combustion peaks substantially, the HCl or water washes should not significantly affect the results.

It was speculated that iron salts removed during the washing procedures were serving as combustion catalysts, and that the combustion peak at the lower temperature shifted and merged with the peak at higher temperatures when those catalysts were removed. To test this hypothesis, minus 60 mesh Illinois No. 6 coal was washed with hot 10% HCl and then with water. After drying the acid-washed coal, aliquots of the coal were spiked with various compounds, including $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , FeCl_3 , FeCl_2 , Na_2SO_4 , Fe_2O_3 , Fe_3O_4 , CaCO_3 , and CaSO_4 . The different iron compounds were added to determine if the oxidation state or mineral form, e.g. oxide versus sulfate, of the iron were important factors affecting catalysis. In separate tests, each of the compounds was mixed dry with an aliquot of the acid-leached coal such that the weight of the compound (including

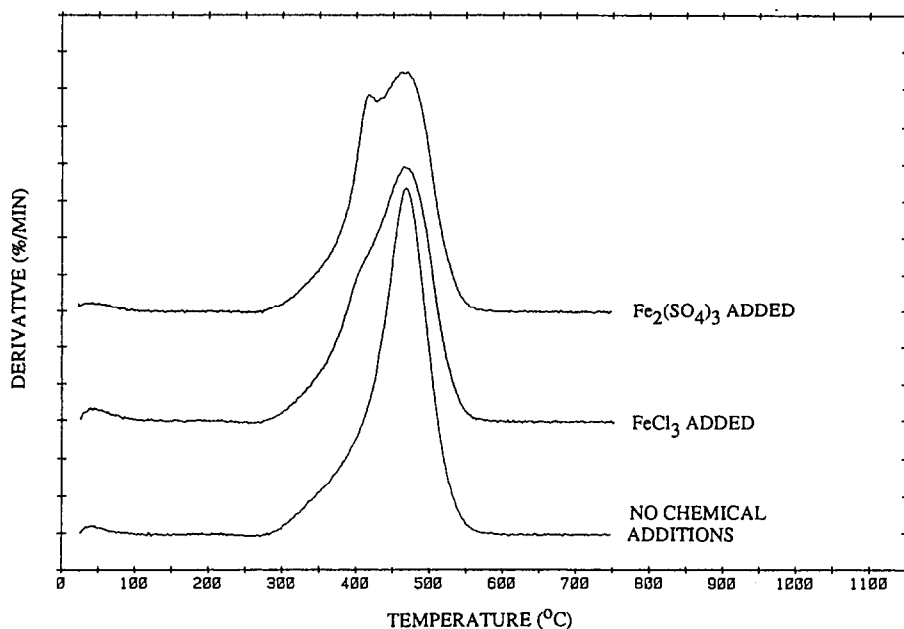


Fig. 7. Burning profiles for acid-leached Illinois No. 6 coal before and after adding aqueous FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$. Profiles are offset vertically for clarity.

waters of crystallization) constituted 3% of the coal weight. In addition to these tests, the iron sulfates and chlorides (one compound per test) were dissolved in water, slurried with the coal, and then evaporated to dryness in an oven at 110°C . As with the tests in which the compounds were mixed dry, the amount of each compound in the individual slurries was chosen so that the compound would be 3% of the coal weight.

Burning profiles for the acid-leached coal before and after impregnation with solutions of FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ are shown in Fig. 7. Although a shoulder appeared on the low temperature side of the combustion peak when FeCl_3 was used, a more prominent effect was evident when $\text{Fe}_2(\text{SO}_4)_3$ was added. In the latter case, a prominent double peak similar to that of the raw coal (see Fig. 5) was observed. Using slurries of FeCl_2 and FeSO_4 affected the burning profiles in the same manner as using FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, respectively. Although the iron sulfates appeared to be slightly more effective catalysts than the iron chlorides, it did not appear to matter whether ferric or ferrous iron was added. Using Na_2SO_4 slurries broadened the peak slightly and shifted it to a slightly lower temperature, but the effects were not nearly as prominent as those observed using the iron sulfates and chlorides.

For the samples that were mixed dry, only FeSO_4 resulted in catalytic effects. It is interesting to note that catalytic effects were observed for the other iron compounds when slurries were used to impregnate the coals,

but not when those compounds were mixed dry. These data indicate that additional tests on the effects of inorganic species on coal burning profiles should be performed. Also, the possibility of synergistic catalytic effects between different inorganic species requires investigation.

It is particularly important to consider catalytic effects in cases where multiple sample-processing steps are used, such as applying a chemical treatment to a coal followed by washing with dilute acid and/or water. Although it may be tempting to conclude that any changes in the burning profiles are due to chemical alteration of the fuel, they may actually be due to the removal of catalytic species during the treatment or washing steps.

Kinetics/thermodynamics

Although TGA/DTG data have been used to obtain kinetic information, there is disagreement as to whether kinetic parameters obtained by this method should be derived from single or multiple heating rates. Some researchers also believe that a single numerical value representing a weighted mean apparent activation energy value is more useful in describing fuel reactivity than the more typical use of several datum temperatures [5]. However, obtaining kinetic parameters from DTG data is controversial and often challenged because kinetic properties are influenced by heating rate and may yield incorrect values for activation energy and reaction order when obtained by DTG [15, 16]. Thus, it is commonly believed that results obtained from burning profiles do not necessarily extrapolate to combustion in a boiler and are not meant to give absolute kinetic or thermodynamic data [2, 6].

CONCLUSIONS

Burning profiles are a valuable tool for examining relative combustion characteristics of fuels. However, interpretation of the burning profiles is not always straightforward. Although bimodal combustion peaks can be caused by many factors, those factors are often not adequately considered when interpreting the data. In cases where multiple combustion peaks are observed, explanations for the multiple peaks should be experimentally verified. In particular, the possibility of catalytic effects may require investigation.

Additional studies on catalytic effects of minerals and inorganic ions on coal reactivity are warranted in view of the diversity of results reported in the literature. As an example, acid washing of some coals appears to affect reactivity by removing catalytic inorganic species, but this effect is not observed for other coals. The importance of such catalytic activity on coal burning profiles has not been adequately defined.

The use of burning profiles to obtain kinetic and thermodynamic data is controversial. In view of the controversy, caution should be exercised when using burning profiles for that purpose.

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