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Combustion studies of coal-derived solid fuels. Part IV. Correlation of ignition temperatures from thermogravimetry and free-floating experiments [1]

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Abstract

The usefulness of TG as an efficient and practical method to characterize the combustion properties of fuels used in large-scale combustors is of considerable interest. Relative ignition temperatures of a lignite, an anthracite, a bituminous coal and three chars derived from this coal were measured by a free-floating technique. These temperatures were correlated with those estimated from TG burning profiles of the fuels.

INTRODUCTION

In producing premium liquids by mild gasification of coal, the principal product is a partially devolatilized coal (char) that must be efficiently utilized (burned or gasified) to improve the overall economics of the process. The loss of volatile matter in a fuel influences its reactivity and combustion characteristics such as ignition, flame stability and carbon burn-out.

Thermogravimetry (TG) has been widely used for evaluating burning properties of coals and chars [1–5]. A plot of the rate of weight loss against temperature while burning a sample in air is referred to as a "burning profile" [2]. Burning profiles obtained under a set of standard conditions provide detailed information from the onset of oxidation to complete burn-out and are useful for predicting the relative ranking of fuels with regard to their combustion reactivities. Fuels which have burning profiles at higher temperatures are more difficult to burn and those with similar burning profiles are expected to have comparable burning characteristics in large coal-fired furnaces [6].

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The usefulness of TG as an efficient and practical method to characterize the combustion properties of a fuel in large-scale combustors is of considerable interest. A good correlation was observed between a fuel's burn-out temperature and its combustion efficiency in a pilot-scale pulverized coal combustor [4]. TG was also used to provide information on the ignition mechanism of coal and char samples [7]. In Part III of this study, combustion efficiencies of a coal and three chars, measured in a laboratory-scale laminar flow reactor (drop tube furnace), were correlated with burning profile burnout temperatures of the fuels [8]. In this paper the "relative" ignition temperature of coals of different ranks and three chars were measured by TG and by a free floating technique. The data obtained by the two methods are discussed and compared.

EXPERIMENTAL

Samples

The samples used in this study included an Illinois bituminous coal (No. 6) and three chars derived from this coal, a lignite and an anthracite. The coal was sample number 1 of the Illinois Basin Coal Sample Bank (IBC-101) [9]. The three chars (MG1, MG2, MG3) were prepared from 150–600 μm IBC-101 coal under mild gasification conditions according to the following procedures: in a fixed-bed reactor of 7.6 cm inner diameter at 550°C, 30 min, under 101 kPa steam (MG1); in a moving-bed reactor at 800°C, 5 min, under 203 kPa nitrogen (MG2); in a fluidized bed reactor of 5.1 cm inner diameter at 630°C, 75 min, under 101 kPa nitrogen. All fuels were ground and sieved to 38–75 μm prior to testing. The analyses of the fuels are presented in Table 1.

Thermogravimetry tests

Burning profiles of the fuels were obtained with an Omnitherm TGA coupled with an Omnitherm QC25 Program/Controller. The TGA system is interfaced with an IBM PC-XT computer through a Keithley DAS series 500 data acquisition system to provide automatic data collection and storage. In a typical run, a sample mass of about 5 mg was heated at a rate of 20°C min^{-1} in a 10%O_2–90%N_2 gas mixture from ambient temperature to 800°C. The flow rate of reactant gas was 200 cm^3 min^{-1}. Under these conditions, thermal runaway, which results from sudden ignition of the sample, did not occur [10]. The percentage weight of the unburned sample, percentage rate of weight loss, and the gas temperature in the vicinity of the sample pan were collected by the computer at 15 s intervals. The percentage rate of weight loss data were plotted against gas temperature to obtain a burning profile.

TABLE 1

Proximate and ultimate analyses of coal, chars, lignite and anthracite (dry basis)

	Coal	MG1	MG2	MG3	Anthracite	Lignite
Moisture	7.9	1.4	2.3	0.8	1.2	37.6
Proximate						
Volatile matter	43.3	13.7	17.9	9.1	6.7 [a]	49.4
Fixed carbon	47.9	73.0	67.5	77.2	86.3	45.0
H-T ash	8.8	13.3	14.6	13.7	2.9	5.5
Ultimate						
Carbon	77.7	76.4	71.2	77.5	89.9	66.1
Hydrogen	5.9	2.6	2.7	1.8	3.5	4.8
Nitrogen	1.4	1.8	1.7	1.8	1.3	0.5
Oxygen (by difference)	1.6	3.0	6.6	2.3	1.4	22.1
Total sulfur	4.6	2.8	3.3	2.8	0.9	1.1
Btu lb^{-1}	13183	12763	12088	12720	14908	11335
Surface area						
N_2-BET	39	3	<1	6	–	–
CO_2-BET	227	293	274	305	–	–

[a] This value was obtained by TG volatile release profile.

Free-floating ignition tests

The ignitability test apparatus, shown in Fig. 1, consists of a horizontal sample tube holder and a vertical quartz reactor tube (2.5 cm × 61.0 cm). The sample holder is connected to an oxygen supply which is controlled by a solenoid valve. Pressurized oxygen is used to inject the sample into the preheated reactor tube. A series of five to seven thin wire (0.076 mm in diameter) type K thermocouples placed along the center axis of the reactor 2 cm apart are used for temperature measurement. By using multiple thermocouples, the approximate location in the reactor where a sample ignites can be identified. The response time of the thermocouples is approximately 5 ms. The thermocouples are interfaced with a computer through a data acquisition system for monitoring the temperatures.

In a typical ignition test, the reactor was heated to a temperature between 350 and 680°C depending on the sample tested. After placing about 20 mg of sample on the sample holder, the reactor was flushed with oxygen ten times. The data acquisition system was set to collect data at 50 ms intervals. The particles were injected into the reactor by manually triggering the solenoid valve. The volume of carrier gas (10 cc at 5–7 psig) was sufficient to ensure that the fuel particles traveled inside the reactor with velocities which approached their free-fall velocities. The mass of sample used, i.e. less than 1000 particles, provided single particle ignition conditions.

Criteria for positive ignition were a brilliant flash and an abrupt increase in temperature inside the reactor during the test. If a negative test was

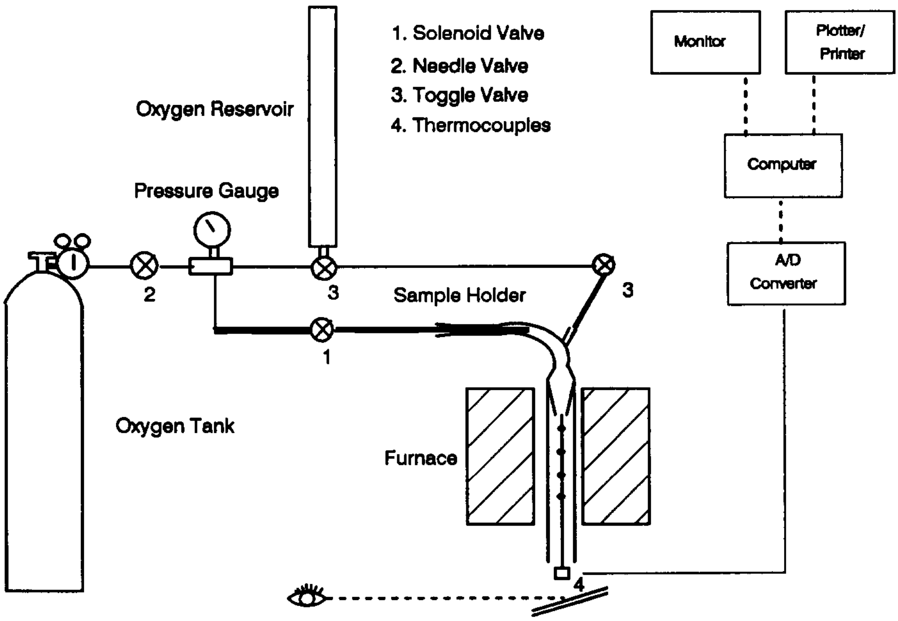

Fig. 1. Ignitability test apparatus.

noted, the reactor temperature was increased in 5°C increments and the test procedure was repeated until positive ignition tests were observed for at least three of five tests, i.e. 60% successful flashes. The standard error in ignition temperature associated with repeat tests was ±10°C.

RESULTS

Burning profiles of the fuels are shown in Fig. 2 and their characteristic temperatures are shown in Table 2. All samples except lignite exhibit a single burn profile. The profiles are generally shifted to higher temperatures with decreasing volatile matter content. The characteristic temperatures defined as the temperatures at the onset of oxidation (T_I) and complete burn-out (T_B) (where the rate of weight loss is 1% min^{-1}) and at peak rate (T_P) are lowest for lignite and highest for anthracite. In this study, T_I was taken as the relative ignition temperature of a fuel under the test conditions. MG2 and IBC-101 have comparable T_P and T_B values, but T_I for IBC-101 coal is 55°C lower than that of the MG2. T_I for coal represents a combined effect of volatile evolution and oxidation as well as char oxidation, while for MG2, T_I represents only the onset of char oxidation. The data suggest the following order for the reactivity of the fuels: lignite > IBC-101 > MG2 > MG1 > MG3 > anthracite. As expected, the reactivities of chars are intermediate between those of anthracite and IBC-101 coal. The faster heating rate and shorter residence time during

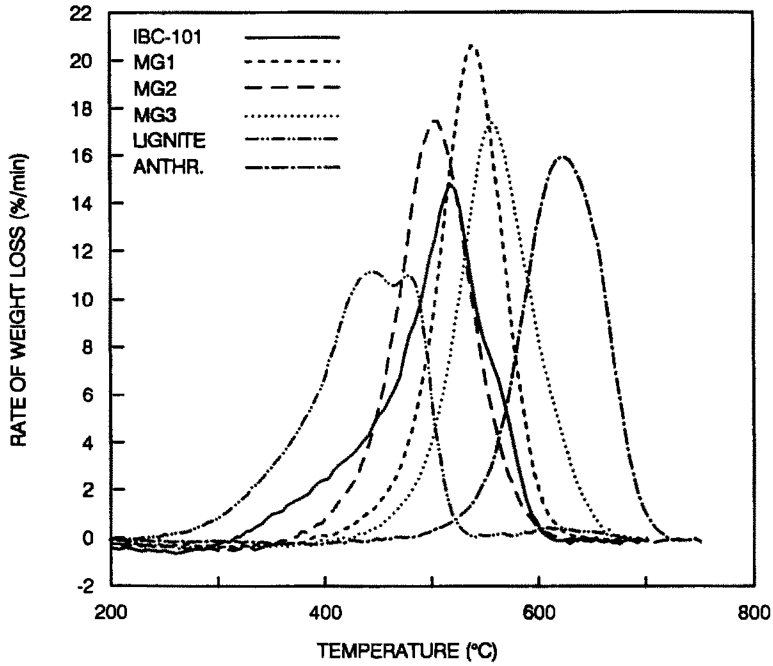

Fig. 2. Burning profiles for fuels.

preparation of MG2 could help explain the higher reactivity observed for this char compared to those of MG1 and MG3 [11].

Figure 3 shows the variation of gas temperature at ignition ($T_{g,i}$) with the volatile matter content of the fuels. The $T_{g,i}$ for a fuel was obtained from temperature–time plots of the thermocouples located in the free-floating ignition reactor. From these plots, the location where ignition took place and the temperature at the onset of a sudden temperature rise ($T_{g,i}$) were obtained. In most cases, ignition occurred 4–6 cm below the injection orifice, and the corresponding temperature rise, depending on the sample, was 300–500°C. As shown in Fig. 3, $T_{g,i}$ generally decreases with an

TABLE 2

Characteristic temperatures for fuel (°C) [a]

	T_I	T_P	T_B
IBC-101	347	508	584
MG1	443	537	605
MG2	402	500	585
MG3	462	555	649
Lignite	312	445	518
Anthracite	528	622	698

[a] All values are averages of two or more tests.

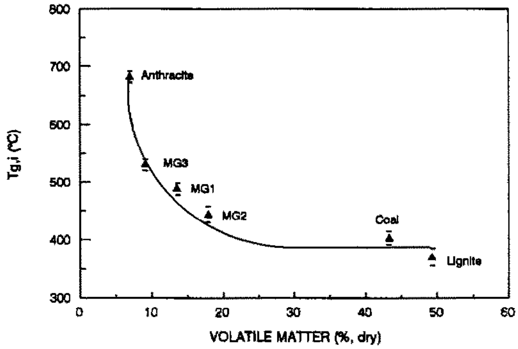

Fig. 3. Ignition temperature (gas) versus fuel volatile matter content.

increase in volatile matter content. Anthracite has a higher ignition temperature than bituminous coal and lignite. The $T_{g,i}$ values for the chars are higher than that of the parent coal sample. The effect of volatile matter on $T_{g,i}$ is less pronounced in the range 25–50% (dry basis). Below 25%, the volatile matter effect on $T_{g,i}$ is significant. The ignition temperature data are in agreement with relative reactivities of the fuel samples as measured by TG. Both methods show a trend of increasing reactivity with increasing volatile matter content. Similar observations have been reported previously [12,13].

The ignition of a single coal/char particle is known to occur either homogeneously by oxidation of evolved volatiles or heterogeneously by direct oxygen attack on the whole particle [13]. The tests conducted in this study were not aimed at evaluating ignition mechanisms. However, several observations can be noted. TG studies of the fuels at 20°C $\min^{-1}$ in nitrogen revealed that the temperatures at the onset of a major weight loss (release of volatile matter responsible for homogeneous ignition) were about 50–100°C higher than the $T_{g,i}$ observed for the three chars, about the same for lignite and IBC-101 coal, and about 150°C lower for the anthracite. At the estimated rates with which particles heat up during ignition tests (10^2–10^3 °C s^{-1}), the onset of volatile release is most likely delayed to temperatures that exceed those of the $T_{g,i}$ for lignite and IBC-101 coal. Based on this argument and the fact that coal particles below 300 μm have been shown to ignite heterogeneously, it can be expected that the ignition of the lignite, IBC-101 coal, and the chars was primarily heterogeneous. For the anthracite, the lowest volatile fuel tested, the ignition is also likely to be heterogeneous.

The $T_{g,i}$ reported for a fuel represents the lowest gas temperature at which ignition was observed. For the ignition of a single small, spherical fuel particle of diameter d, injected into an oxidizing atmosphere of temperature $T_{g,i}$, the following relationships have been established [13]:

$$T_{P,i} = [\alpha/(\alpha-2)]^{1/2} T_{g,i} \qquad (1)$$

and

$$T_{g,i}^{\alpha-2} d P_g^n = \text{constant} \tag{2}$$

where $T_{P,i}$ is the particle temperature at ignition, P_g is the partial pressure of oxygen, n is the reaction order, and the parameter α is a constant for a given fuel which is obtained from the slope of the log–log plot of $T_{g,i}$ against d for several size fractions of a fuel. $T_{P,i}$ values were calculated for the coal based on the $T_{g,i}$ values obtained for three size fractions (38–53, 53–75 and 100–150 μm). The $T_{g,i}$ values were 431, 411 and 386°C, respectively, and were about 40°C lower than $T_{P,i}$ for each of the size fractions. The observed decrease in $T_{g,i}$ with increasing particle size is in agreement with the single particle ignition assumption, i.e. eqn. (2). The $T_{P,i}$ values were not calculated for the other fuels. However, the values of $T_{P,i}$ for three chars prepared from the same coal used in this study (char preparation conditions are reported in ref. 8) were between 22 and 60°C higher than $T_{g,i}$, depending on the volatile matter content of the chars which ranged from 8 to 15% (dry basis).

In Fig. 4, $T_{g,i}$ values are compared with T_I obtained from TG burning profiles (Fig. 2). A definite linear correlation exists between the two temperatures, with $T_{g,i}$ higher than T_I. The anthracite does not follow this correlation. On the basis of visual observations, this sample ignited differently from the other samples tested, i.e. for this sample, a small, low intensity flash of light was observed during free-floating experiments.

Correlations such as that shown in Fig. 4 could have practical applications when a large database is established for different types of fuel with known ignition and burning properties in larger coal-fired boilers. These correlations can provide useful information about the relative ignitability of new fuels compared to those with known performances under boiler conditions.

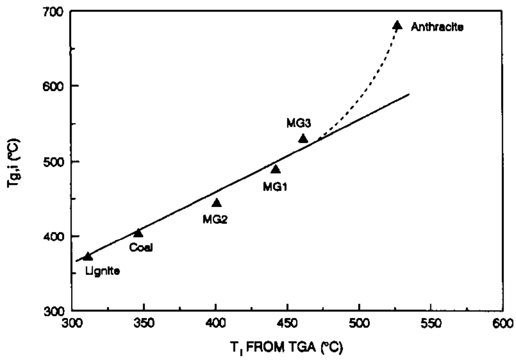

Fig. 4. Comparison of T_I from burning profile and ignition temperature.

CONCLUSIONS

The preliminary results presented in this paper should encourage thermal analysts, boiler engineers and coal scientists to investigate further the potential of TG as a rapid and cost effective technique to predict combustion characteristics of fuels under conditions representative of coal-fired boilers. Future experiments should correlate ignition temperature in the flame and ignition time with TG reactivity data. Measurements in continuous flow experiments (drop tube furnace) which relate gas temperature to carbon burn-out and gas composition are highly desirable.

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