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A THERMAL ANALYSIS STUDY OF THE OXIDATION OF BROWN COAL CHARS

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The combustion of brown coal chars, obtained at different pyrolysis temperatures, have been investigated using TG, DTG and DTA thermal analysis methods. The burning profiles and the kinetic parameters derived from TG and DTA data show that all the chars are less reactive than the parent coal. The higher temperature chars have lower overall reactivity. From the corresponding infrared spectra, the chars obtained at 800 °C and 1000 °C appear to have graphitic structures.

Victorian brown coal is a low rank, non-coking coal which produces a char during the pyrolysis process. Brown coal char is mainly used in the manufacture of acetylene for the plastics industry [1]. The properties of char depend on the conditions of pyrolysis via which it is produced.

Thermal analysis offers an attractive and rapid method for the investigation of the char oxidation process. The DTA curve reflects the magnitude of the enthalpy change during combustion [5], and the TG and DTG profiles can be used to derive corresponding kinetic parameters [2–10].

Several studies have been reported [2, 4] on the reactivity of bituminous coal char using isothermal TG techniques. The results obtained by Khan [2] suggest that low-temperature chars exhibit higher reactivity than the parent coal or high-temperature chars and that the oxygen chemisorption capacity is an important reactivity parameter. Patel et al. [7] studied the combustion rate of lignite char by isothermal methcds. The activation energy obtained in the chemical rate controlled zone was 120 kJ/mol. Compared to isothermal analysis, non-isothermal analysis has some advantages [12]. One mass loss curve is equivalent to a large number of isothermal mass loss curves and only one sample is required. The kinetics of oxidation can be derived over the entire relevant temperature range.

Victorian brown coal and char are highly reactive with oxygen. It is very difficult to use isothermal techniques to investigate the oxidation kinetics, because the

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sample reacts immediately upon exposure to oxygen and the combustion reaction is so exothermic that the temperature of sample exceeds that of the furnace.

In this study, the combustion characteristics of brown coal char have been investigated using TG–DTA and relevant kinetic parameters have been derived for the char combustion process.

Experimental

Chars produced from Victorian brown coal at different pyrolysis temperatures in a laboratory tube furnace were investigated using the Rigaku–Denki, Type 8085 (Thermoflex) TG–DTA Thermal Analysis System employing the following conditions: atmosphere, static air; sample size, 5 mg; heating rate, 20 deg/min; platinum crucibles; inert reference, Al_2O_3; particle size, less than 80 mesh (< 175 μm). All samples were air dried. The proximate analysis data for the char samples and the parent coal are listed in Table 1. The infrared spectra of the brown coal and char samples were obtained using the KBr disc technique. Discs (100 mg) contained about 0.5% of sample. The spectra were obtained over the range 400–4000 cm^{-1} using a Perkin–Elmer 1430 Ratio Recording Infrared spectrophotometer.

Results and discussion

Burning profiles

Figures 1 and 2 show the TG and DTG curves of the char samples investigated. From these curves, the mass loss prior to 200° is primarily due to moisture loss from the chars. Above 250°, the mass of some char samples, particularly the low

Table 1 The proximate analysis of brown coal and the corresponding chars

Sample	Moisture % ad	Proximate-% d.b.		
		VM	*A*	*FC*
1000 °C char	9.2	3.6	4.9	91.5
800 °C char	6.5	3.7	4.4	92.0
600 °C char	2.4	12.0	3.0	84.9
500 °C char	2.5	22.6	3.0	74.3
400 °C char	5.4	31.0	3.0	65.9
Loy Yang coal	15.6	51.7	1.1	47.2

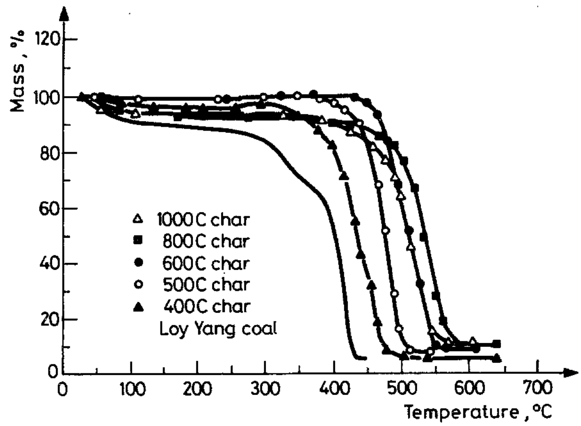

Fig. 1 TG curves of the combustion of brown coal chars

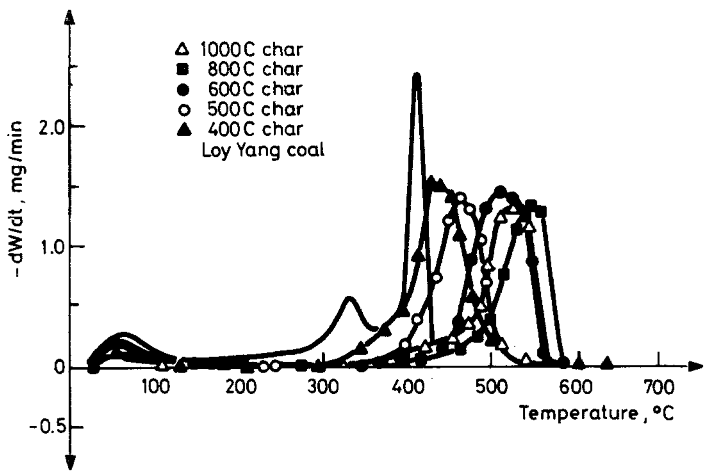

Fig. 2 DTG curves of the combustion of brown coal chars

temperature chars (< 600°), initially increases and then decreases with increasing temperature. At the ignition point $T_{i.g}$, the sample ignites and thence, the rate of oxidation of the char increases rapidly until a maximum rate R_m is attained, thence the remainder of the char rapidly burns off.

For the oxidation of brown coal, there was no detectable mass gain during the entire process [11]. With the oxidation of chars, the small mass gain shown on the TG curve suggests that some adsorption of oxygen occurred on the char surface. This was subsequently followed by the oxidation of the chars with a further increase in temperature. The magnitude of adsorption of oxygen by the chars decreases with the temperature of char formation.

Table 2 Characteristics of the oxidation of brown coal chars

Sample	T_i, °C	T_m, °C	T_b, °C	R_m, mg/min	E, kJ/mol	ln A
1000 °C char	475	527	570	−1.3	195	29.2
800 °C char	488	542	587	−1.32	208	30.5
600 °C char	462	511	567	−1.44	191	28.6
500 °C char	397	447	541	−1.42	134	21.0
400 °C char	393	440	538	−1.53	119	19.4
Loy Yang coal	292	409	448	−2.42	—	—

Some characteristics derived from the TG, and DTG curves are listed in Table 2. The ignition temperature $T_{i.g}$ is taken as the extrapolated onset $T_{e.o}$ on the TG curve and the temperature T_m at which the maximum rate of oxidation R_m occurs is taken as the peak temperature on the DTG curve. The ignition temperatures $T_{i.g}$ of chars are higher than that of the parent coal because the volatile matter content of char is much less than that of the parent coal. The $T_{i.g}$ and T_m of the chars increase with the temperature of char formation, with the exception of the 1000° char. The $T_{i.g}$ and T_m for this char are lower than those of the 800° char.

Generally, the DTA curves of brown coal show the main peak proceeded by a small peak or shoulder which is related to the loss of volatile matter from the coal [11]. These minor peaks are largely decreased or absent in the DTA curves of the corresponding chars. Most of volatile compounds in brown coal have been removed from the chars during the carbonization process. The combustion profiles of the chars are much simpler than those of the corresponding parent brown coal. In Fig. 3, the DTA curve of the 400° char shows a shoulder proceeding the main peak and is due to the incomplete release of the volatile matter. Chars obtained at 500, 600, and 800° only show a main combustion peak. The oxidation of the 1000° char is different from that of the other chars since the corresponding burning profile appears in a lower temperature region than that of 800° char. There is also a small shoulder on the main peak of this profile.

Reaction kinetics

It is assumed that the oxidation of char is a first order reaction and that the Arrhenius equation is obeyed. Hence:

$$\frac{dW}{dt} = kW \tag{1}$$

and

$$k = a \cdot e^{-E/RT} \tag{2}$$

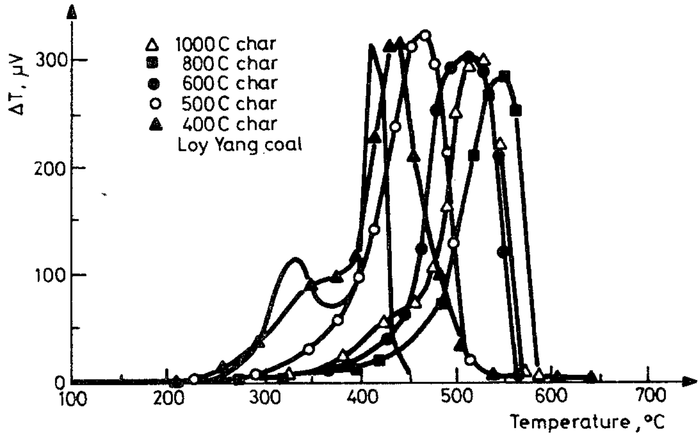

Fig. 3 DTA curves of the combustion of brown coal chars

where W is the mass of the residual char sample (mg); k is the rate constant: A is the apparent frequency factor (1/min); R is the gas constant (kJ/K/mol); T is the absolute temperature (K); and E is the apparent activation energy (kJ/mol). From Eqs (1) and (2), the following equation is obtained:

$$\ln\left(-\frac{1}{W}\frac{\mathrm{d}W}{\mathrm{d}t}\right) = \ln A - \frac{E}{RT} \tag{3}$$

Plots of $\ln(-\mathrm{d}W/\mathrm{d}t \cdot 1/W)$ and $1/T$, as derived from TG and DTG data, are shown in Fig. 4. The relationships for all the chars are linear (with $r \geqslant 0.99$) which

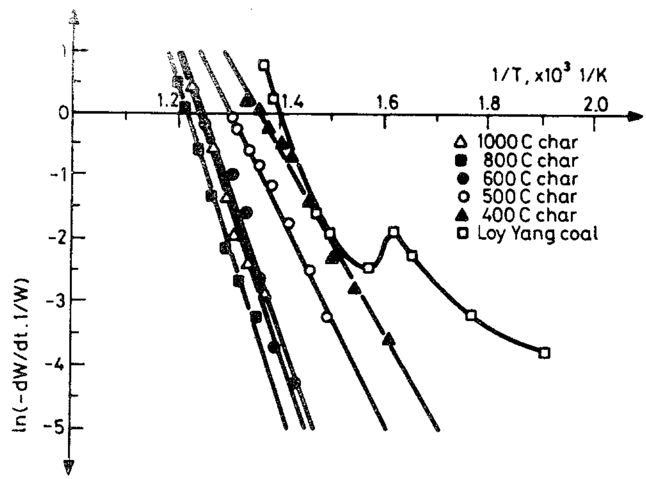

Fig. 4 Arrhenius plots of the combustion of brown coal chars

suggests that Eq. (3) is valid. However the plot for Loy Yang coal is curved with a peak at the same temperature as that of the first peak on DTG curve. Hence for the low rank coal, the Arrhenius expression is invalid due to the associated high volatile matter content.

From Fig. 4, the activation energy E is calculated from the slope of the straight line and ln A from the intercept. The values of E and ln A for all the char samples investigated are shown in Table 2. The activation energy varies in the range 110 to 210 kJ/mol and is higher for higher T_i and T_m.

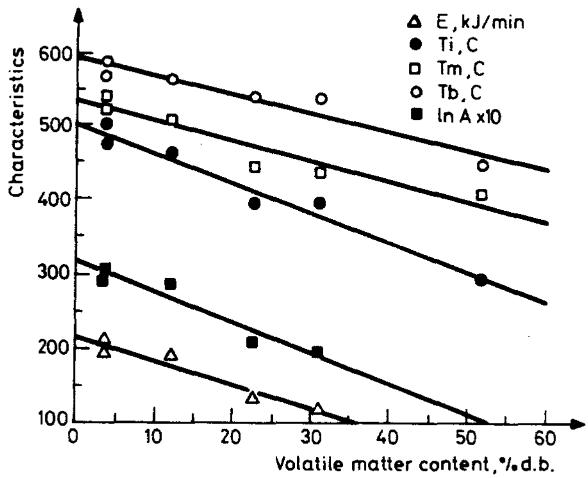

Fig. 5 Characteristics of char combustion from TG–DTG data

Figure 5 shows the relationship between the oxidation characteristics and volatile matter contents. All the characteristics T_i, T_m, T_b, R_m, E and ln A increase with decreasing volatile matter content. Hence, for the char with lower volatile matter content (higher temperature of formation), the reactivity is lower.

Infrared spectra

The infrared spectra of the parent coal and chars investigated are presented in Fig. 6. The assignments are based on literature data [1, 13–16], and are given in Table 3. The spectra of the 400° and 500° chars are similar to that of the parent coal. However, due to the release of volatile matter, the intensities due to certain functional groups, such as, aliphatic CH, C=O, C—O, O—H, etc. are decreased. For the 600° char, some characteristics of the parent coal have disappeared only some aromatic CH is still remained. The chars obtained at 800 and 1000° possess little resemblance to the parent coal. The corresponding spectra are similar to that

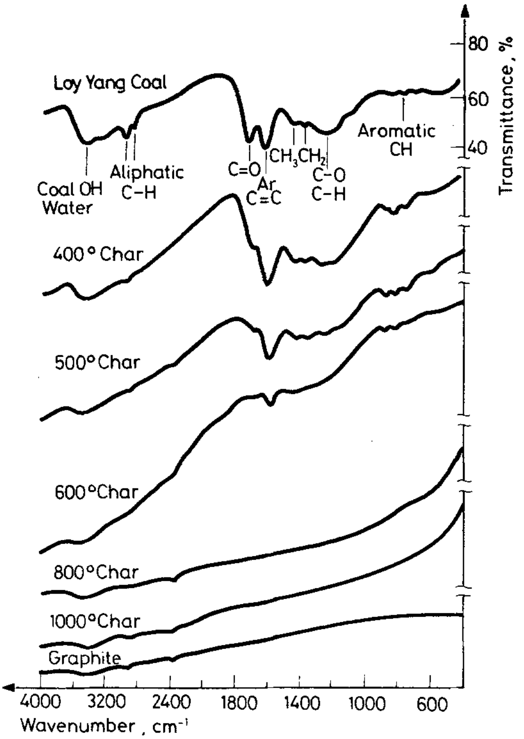

Fig. 6 The infrared spectra of brown coal and the corresponding chars

Table 3 Infrared analysis of brown coal and the derived chars

Characteristic band cm^{-1}	Assignment
3400	Associated OH
2920	Aliphatic CH
2860	Aliphatic CH
1710	Carbonyl group C=O
1615	Aromatic ring C=C
1450	Aliphatic CH_2 and CH_3 groups
1380	CH_3 group cyclic CH_2 group
1275 to 1175	C—O, aromatic ring OH
875	Four adjacent CH groups on benzene ring
820	Two adjacent CH groups on benzene ring
770	Isolated CH groups on benzene ring

of graphite. From Fig. 6, the structures of the chars pyrolysed at 800° and higher temperatures are quite different to the structure of parent coal, consistent with a change of structure from aromatic to graphitic. Hence, the combustion properties are quite different.

Conclusion

1. The oxidation reactivities of chars as derived from Loy Yang coal are less than those of the parent coal. The characteristics of oxidation as derived from TG, DTG and DTA results indicate that the reactivity of char is related to the volatile matter content. For the char produced at a higher pyrolysis temperature, the volatile matter content is lower and the reactivity is lower.

2. The oxidation of char is consistent with first order kinetics and the Arrhenius equation is obeyed. The activation energies of overall char oxidation are derived from TG–DTG results and these range from 110 to 210 kJ/mol.

3. The DTA curves of chars are much simpler than that of parent coal. The DTA curve of brown coal has two separate peaks with the first related to the release of volatile matter which is decreased or absent on the DTA curves of chars.

4. The infrared spectra show that the higher temperature chars possess few structural characteristics of the parent coal. Many functional groups have been removed from the chars during the pyrolysis process. The structure of coal has essentially changed from aromatic to graphitic.

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Zusammenfassung — Mittels TG-, DTG- und DTA-Methoden wurde die Verbrennung von unter verschiedenen Pyrolysetemperaturen erhaltenen Braunkohlenschwelkoksen untersucht. Das Verbrennungsprofil und die kinetischen Parameter, erhalten aus TG und DTG, zeigen, daß die Schwelkokse eine geringere Aktivität haben, als die ursprüngliche Braunkohle. Die Schwelkokse höherer Temperatur besitzen eine niedrigere resultierende Aktivität. Aufgrund der entsprechenden IR-Spektren besitzen die bei 800 °C und 1000 °C erhaltenen Schwelkokse eine Graphitstruktur.

Резюме — Методом ТГ, ДТГ и ДТА изучено горение обожженных образцов лигнита, полученных при различных температурах пиролиза. Профили их горения и кинетические параметры, установленные из данных ТГ и ДТГ, показали, что все обожженные образцы обладали меньшей реакционной способностью по сравнению с исходным углем. Образцы, обожженные при более высоких температурах, обладали еще более низкой реакционной способностью. Как показали ИК спектры, образцы, полученные при 800 и 1000°, обладают структурой графита.