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Rate Analysis of Oxidation of Low Rank Coals Covering Whole Combustion Range using DAEM and Constant Temperature Oxidation Methods.

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Highlights
- Heat generation rates of low rank coals by oxidation at as low as 50 °C were formulated.
- The heat generation rate equations allows the estimation of spontaneous combustion of coal.
- The DAEM proposed by the authors was successfully applied for the kinetic analysis.
- Novel insight was presented for both spontaneous combustion and combustion of coal.

1. Introduction

Analysis of coal oxidation at low temperature is essential for estimating propensity degree to spontaneous combustion. Analysis of oxidation rate of volatile components at low temperature is also important for estimating combustion efficiency of low rank coal. Those rates cannot be estimated from the weight change rates, because the weight changes at low temperatures are too small to be detected. This work successfully measured the heat generation rates at the low temperature region using a TG-DSC analyzer. With the aid of the distributed activation energy model proposed by the authors [1], the heat generation rates of the low temperature region were successfully formulated. These results are expected to give new insights on spontaneous heating and combustion of coal.
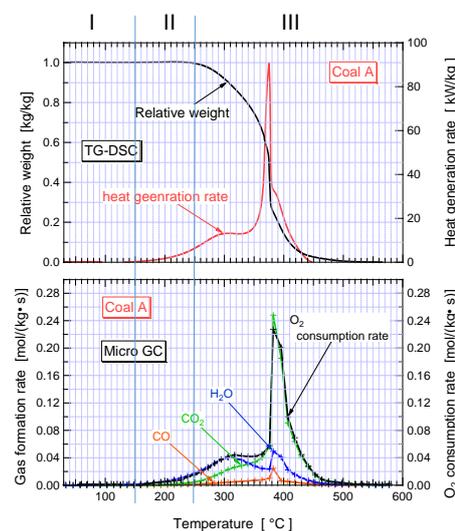
2. Methods

Indonesian lignites, Pendopo (PD) and coal A, and an Australian brown coal, Loy Yang (LY), were used as low rank coals. A TG-DSC analyzer (NETZSCH, STA 449F3) was used for simultaneous measurements of weight change and heat flow during the oxidation of coal in a dry air stream. Temperature programmed reaction (TPR) at constant heating rates of a = 5, 10, 20, and 30 K/min measured both weight changes and heat generation rates between 40 and 600 °C. Constant temperature oxidation experiments were also performed at 50, 70, 90, 107, 120, 135, and 150 °C. The gas formation rates of H_2O, CO_2, and CO were measured by using a micro gas chromatograph (Varian, CP4900) directly connected to the TG-DSC analyzer.

Figure 1 shows an experiment performed at a = 10 K/min for Coal A using about 15 mg of sample (d.a.f. basis). It is clearly shown that changes of all properties are very small below 150 °C, that only heat generation is clearly detected at 150 to 250 °C, and that changes of all properties are clearly measured. Then the oxidation reaction was analyzed by dividing the temperature region into three stages as follows:

Figure 1. Typical result obtained by TPR experiment.

Stage I (T_C < 150 °C): Since TPR experiments are not applicable, constant temperature oxidation experiments measuring heat generation rates were employed [2].

Stage II (100 °C < T_C < 250 °C): Heat generation rates measured by the TPR experiments were used.

Stage III (T_C > 250 °C): Weight changes data measured by the TPR experiments were used.

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2. Analysis of stages II and III by using DAEM [1]

We assume that the oxidation reaction of coal consists of many first order reactions j-th reaction of which can be represented by

$$-\frac{\mathrm{d}W_j}{\mathrm{d}t} = k_{0j}(p_{O_2})\mathrm{e}^{-E_j/RT}W_j \tag{1}$$

where W_j the weight of reaction species, k_0 the frequency factor, E the activation energy, and the subscript j indicates the j-th reaction. The overall relative weight, W/W_0, can be obtained by summing up Eq (1) over all reactions to give [1]

$$1 - W/W_0 = \int_0^\infty \exp(-k_0 \int_0^t \mathrm{e}^{-E/RT}\mathrm{d}t)f(E)\mathrm{d}E \tag{2}$$

where $f(E)$ a normalized distribution function of E.

The accumulated amount of heat generated by the j-th reaction, Q_j, can be given using the reaction enthalpy, $\Delta H_{R,j}(T)$, by

$$Q_j = (-\Delta H_{R,j}(T))(W_{j0} - W_j) = Q_{j0} - \Delta H_{R,j}(T)W_j \tag{3}$$

Combining Eqs (1) and (3) gives the heat generation rate of the j-th reaction, $\mathrm{d}Q_j/\mathrm{d}t$, by

$$\frac{\mathrm{d}Q_j}{\mathrm{d}t} = k_{0j}(p_{O_2})\mathrm{e}^{-E_j/RT}(Q_{j0} - Q_j) \tag{4}$$

The overall relative accumulated amount of heat generated, Q/Q_0, can be obtained by summing up Eq (4) over all reactions to give

$$Q/Q_0 = \int_0^\infty \exp(-k_0 \int_0^t \mathrm{e}^{-E/RT}\mathrm{d}t)f(E)\mathrm{d}E \tag{5}$$

Experimentally obtained relationships of either W/W_0 vs. T or Q/Q_0 vs. T at three different constant heating rates of a allow to estimate both k_0 and E at same W/W_0 or Q/Q_0 values by using

$$\ln(\frac{a}{T^2}) = \ln\frac{k_0 R}{E} + 0.6075 - \frac{E}{R}\frac{1}{T} \tag{6}$$

(a) Stage I   (b) All stages

Figure 2. Rate parameters estimated for two coals.

3. Analysis of stages II and III by using DAEM

Figure 2 shows the rate parameters estimated for all oxidation stages. Oxidation reaction at Stage 1 was successfully analyzed by three first order reactions, and both Stage II and II were analyzed by the DAEM method shown above. It was found that both k_0 and E change continuously with the progress of oxidation.
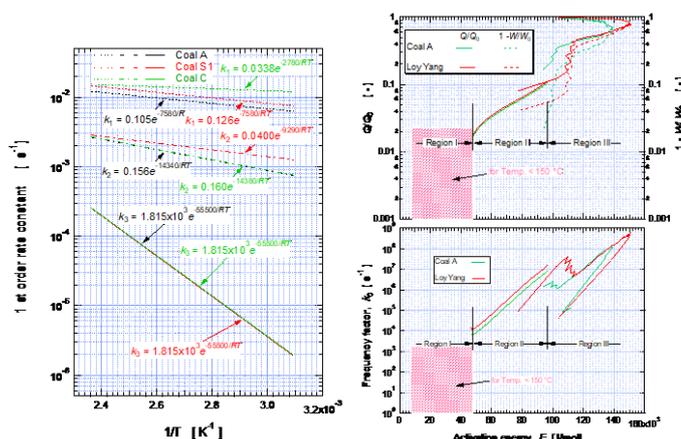
4. Conclusions

Air oxidation experiments of low rank coals ranging from 40 to 600 °C were performed using a TG-DSC analyzer by a TPR method. Three reactions with the activation energies, E, of 7 to 46 kJ/mol below 150 °C, several reactions with $E = \sim50$ to ~100 kJ/mol at 150 to ~280 °C, and two reactions with $E = 100\sim110$ kJ/mol and $40\sim150$ kJ/mol over ~280 °C were found to represent the oxidation of two low rank coals.

References

[1] K. Miura, T. Maki, Energy Fuels. 12 (1998) 864-869.
[2] K. Miura, H. Ohgaki, N. Sato, M. Matsumoto, Energy Fuels. (2017) DOI:10.1021/acs.energyfuels.7b01817.