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出版情報：Carbon Reports. 4 (1), pp.81-88, 2025-03-01. 炭素材料学会
バージョン：

Research Paper
Carbon Reports
Vol. 4 No. 1 2025 81-88

Reducing the spontaneous combustion and analysis of the oxidation reaction kinetics of brown coal upgraded by oxidation treatment

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To optimize the use of brown coal, methods for minimizing the spontaneous combustion of upgraded brown coal were investigated. Previous studies have shown that the controlled oxidation at 200–240 °C of Loy Yang coal from Australia, a typical brown coal, stabilized the functional groups of the coal which significantly reduced its ignition potential to the level of bituminous coal. However, the influence of the oxidation conditions on further reducing the spontaneous combustion potential of the upgraded coal was not thoroughly assessed. In this study, the exothermic reaction rate during the oxidation of upgraded Loy Yang coal was carefully examined. Its weight change and heat generation rates were measured during oxidation at temperatures between 140 °C and 300 °C, with O_2 concentrations of 1–15 vol%, using thermogravimetry-differential scanning calorimetry. The exothermic reaction was identified as an apparent first-order reaction in the temperature range of 140–240 °C, and the heat generation rate was described by an Arrhenius-type equation. The activation energy was found to be approximately 60 kJ/mol, with the O_2 concentration affecting the frequency factor. Based on these results, a new equation was proposed to predict the oxidation conditions of the upgraded brown coal.

KEYWORDS : Brown coal, Oxidation treatment, Reaction kinetics, Spontaneous combustion, Upgraded coal

1. Introduction

In recent years, coal prices have experienced significant fluctuations due to rising demand and the impact of political conflicts [1, 2], making it challenging to secure a stable and low-cost supply of coal. Consequently, the use of low-rank coals, which are abundant and affordable, as an alternative to bituminous coal has been considered for power generation [3]. However, Loy Yang coal (brown coal) from Victoria, Australia, a typical low-rank coal, contains approximately 60 wt% moisture, with volatile components comprising roughly half of the remaining 40 wt% [4]. This results in a low heating value per unit weight, necessitating an upgrading (carbonization) process for use in conventional boilers [3]. While some volatile components must remain during the upgrading process to maintain combustibility, the dried and upgraded coals, which still contain volatile matters, are highly pyrophoric, complicating their transport and storage. Therefore, developing a method to prevent spontaneous combustion of upgraded coal is indispensable for the effective utilization of low-rank coal.

Coal contains oxygen-containing functional groups and aliphatic hydrocarbons [5–10], and spontaneous combustion is thought to result from moisture adsorption onto these functional groups [11, 12] and/or heat generation from the oxidation of aliphatic hydrocarbons [13–17]. **Fig. 1** illustrates a typical heat generation process due to coal oxidation [17]. It has been reported that the reaction producing carboxyl groups, one of the oxidation reactions depicted in **Fig. 1**, generates a large amount of heat [18]. Through quantum chemical calculations, we have also confirmed that carboxyl groups and esters are chemically more stable than aliphatic hydrocarbons, with the latter being converted to carboxyl groups and esters during oxidation treatment at 200–300 °C [19]. Additionally, we have demonstrated that the spontaneous combustion of the oxidized upgraded low-rank

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https://doi.org/10.7209/carbon.040108
(Received November 6, 2024, Accepted December 26, 2024)
(J-STAGE Advance published January 7, 2025)

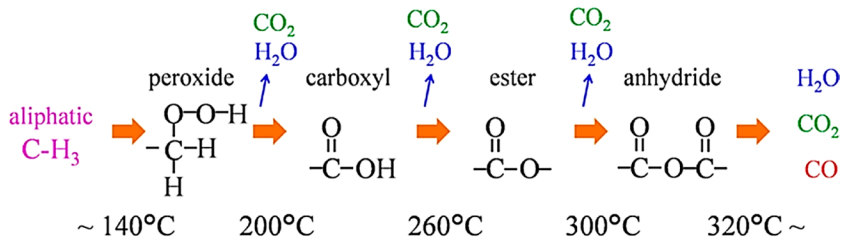


Fig. 1 Proposed scheme for the change of the functional groups of coal through oxidation reactions [17] (Reprinted with permission {H. Fujitsuka, R. Ashida, M. Kawase, K. Miura, Examination of low-temperature oxidation of low-rank coals, aiming at understanding their self-ignition Tendency, Energy & Fuels, 2014, 28(4): 2402–2407}. Copyright (2014) American Chemical Society).

Table 1 Composition of the coals used in this study.

Coal		Ultimate analysis [wt%, dry]					Proximate analysis [wt%, dry]			Higher heating value [kcal/kg]
		C	H	N	O	S	Ash	VM	FC	
Loy Yang	Raw coal	68.0	4.8	0.7	23.2	0.3	2.5	50.0	47.4	6403
	Upgraded coal	78.1	3.4	0.8	14.2	0.3	3.2	23.3	73.6	7312
Subbituminous coal A		70.1	5.1	1.1	20.3	0.1	3.9	47.0	49.2	6699
Bituminous coal B		71.6	4.4	1.8	9.6	0.5	13.5	33.1	53.4	7038

coal exposed to dry air was significantly reduced compared to that of bituminous coal [19].

Nevertheless, the impact of oxidation treatment conditions on curtailing the spontaneous combustion of the upgraded coal has not been fully understood. Furthermore, as oxidation treatment is an exothermic reaction, evaluating the rate of the oxidation reaction is crucial for selecting the appropriate reaction process and controlling temperature runaway during industrial oxidation treatment. This study utilized upgraded coal from Loy Yang coal, which was processed to achieve a heat value comparable to that of bituminous coal, to investigate the optimal oxidation treatment conditions for reducing spontaneous heat generation, with variations in temperature and O_2 concentration. Efforts were also made to determine the reaction rate equation describing the oxidation treatment.

2. Experimental

2.1 Weight change and heat value of the upgraded coal during the oxidation treatment

A series of experiments was conducted using a thermogravimetry-differential scanning calorimetry (TG-DSC; NETZSCH, STA 449F3) instrument, which simultaneously measures weight changes and heat values. Loy Yang coal was crushed to a particle size of 212 μm and dried in a thermostatic chamber at 107 °C for 3 h. A 15-mg sample of the resultant dried coal was placed in a platinum cell (8 mm φ×5 mm H) and heated to 465 °C at a rate of 10 °C/min under N_2 atmosphere, where it was held for 60 min for carbonization to prepare the upgraded coal. The upgraded coal was cooled to the desired temperature without being removed from the apparatus. Once the temperature stabilized at the target value (140, 200, 240, 260, and 300 °C), the N_2 gas flow was replaced with a mixture of N_2 with O_2 at concentrations of 1.0, 2.5, 5.0, 10.0, and 15.0 vol%. Subsequently, the oxidation treatment was performed for 60 min, during which the weight change and heat value were recorded.

2.2 Evaluation of the heat generation of oxidation-treated upgraded coal

Upon completion of the oxidation treatment, the gas flow was switched back to N_2 without removing the sample from the apparatus, and the sample was cooled to 107 °C. Once the temperature stabilized at 107 °C, the atmosphere was changed to dry air and the heat value of the oxidized upgraded coal was assessed. The 107 °C temperature was chosen to simulate the exothermic properties of coal in its dry state, corresponding to the coal drying temperature specified by the JIS standard (JIS M 8812).

3. Results and Discussion

Table 1 presents the results of the proximate analysis, elemental analysis, and heat value of the raw and upgraded Loy Yang brown coals used in the test, along with raw subbituminous coal and raw bituminous coal for reference. Although the upgraded coal used in the following experiments was prepared by carbonization in the TG-DSC apparatus, the data for the upgraded coal in **Table 1** corresponds to the specimen prepared in a tubular electric furnace under the same conditions. Compared to the raw coal, the upgraded coal had a volatile matter (VM) content reduced to less than half, an increased carbon content, and a heat value that surpassed that of the subbituminous coal, reaching a level comparable to that of bituminous coal.

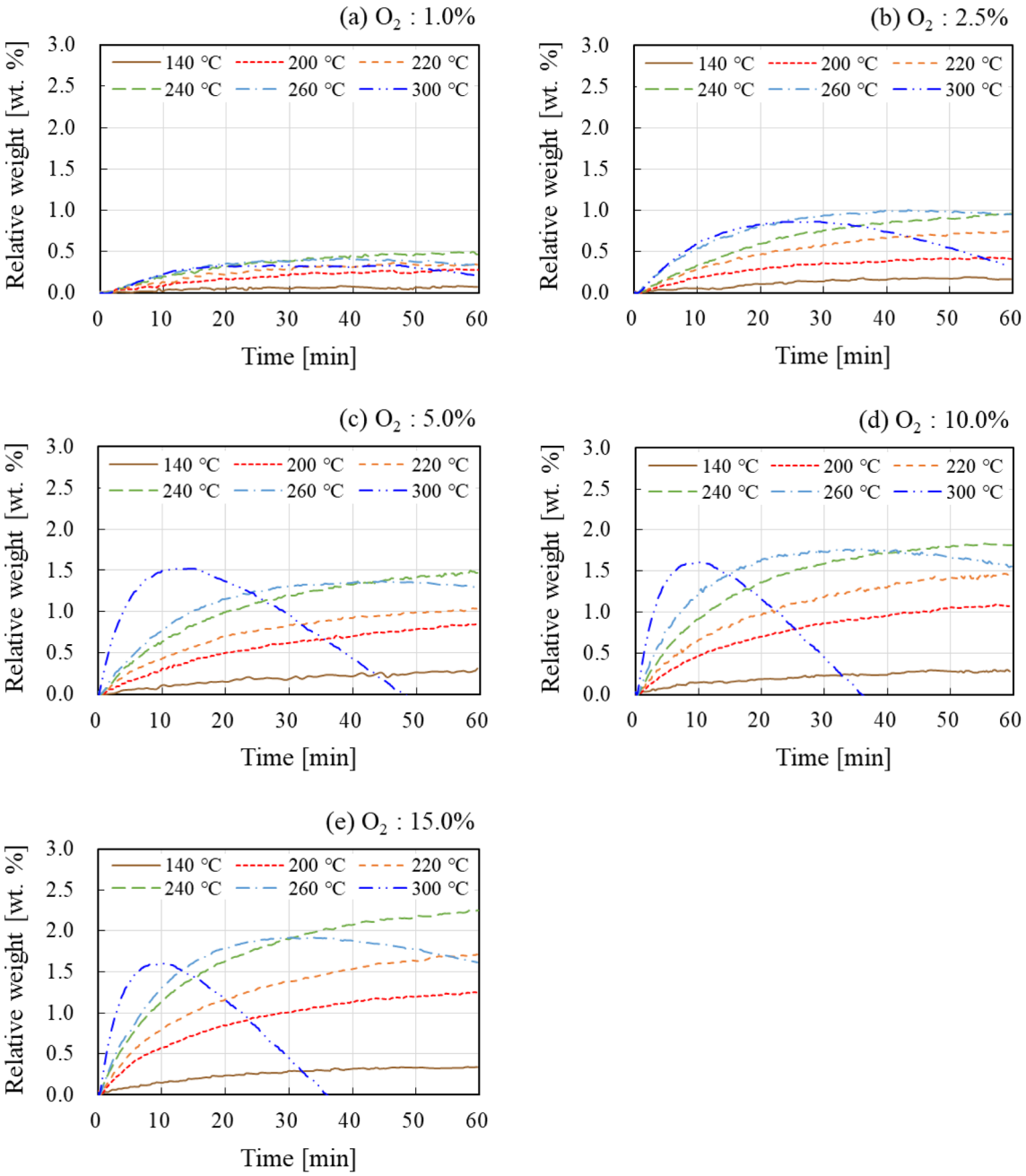


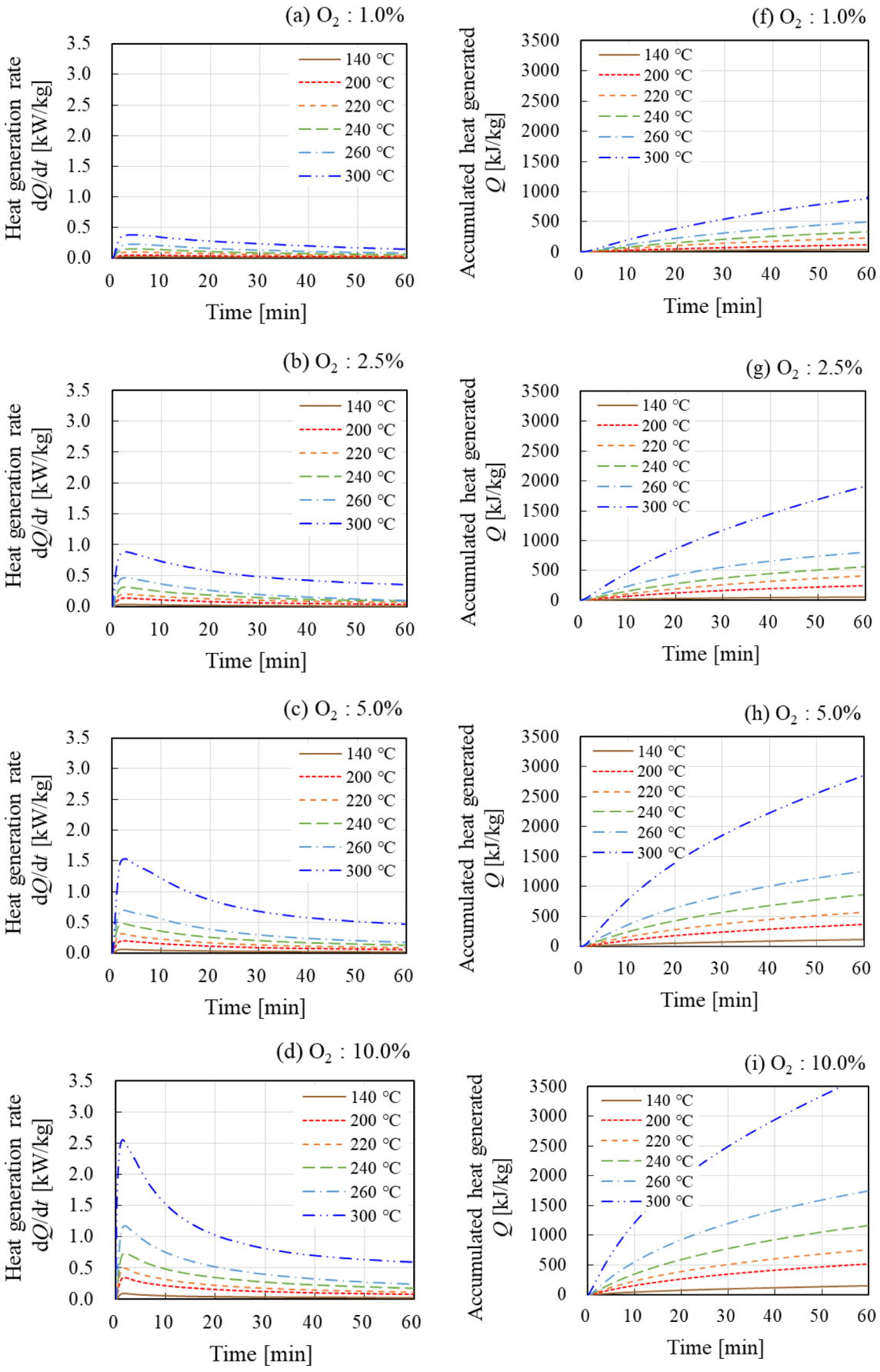
Fig. 2 Changes in the weight of the upgraded brown coal during oxidation treatment at different temperatures and O_2 concentrations.

3.1 Oxidation reactivity of the upgraded coal during the oxidation treatment

Fig. 2 illustrates the weight change during the oxidation treatment of the upgraded coal. The weight tended to increase because of the treatment, suggesting that oxygen was incorporated into the functional groups of the upgraded coal, resulting in oxidation. This weight increase occurred more rapidly at higher oxidation treatment temperatures, with the most significant rise observed at 300 °C. Up to 240 °C of the oxidation treatment temperature, a monotonic weight increase was observed, but above 260 °C, a peak was observed. This is likely due to the excess oxidation of the functional groups of the upgraded coal above 260 °C, causing partial gasification into CO, CO_2, and H_2O. Additionally, this tendency became more pronounced as the O_2 concentration increased, suggesting that the amount of O_2 supplied during oxidation is one of the dominant factors.

Fig. 3 depicts the heat generation behavior of the upgraded coal during oxidation treatments at various temperatures and O_2 concentrations. **Fig. 3**(a)–(e) present the instantaneous heating values per unit time, while **Fig. 3**(f)–(j) show the time-integrated values, representing the total heat generated over the duration of the treatment.

Heat was produced under all oxidation treatment conditions, confirming that the oxidation of the upgraded coal is exothermic. The heat value was high during the initial 10 min after the introduction of O_2 but stabilized within 30 min. Subsequently, the rate of heat generation gradually decreased, although it continued for at least 60 min throughout the oxidation treatment. Additionally, the heat


(a) O2 : 1.0%
(b) O2 : 2.5%
(c) O2 : 5.0%
(d) O2 : 10.0%
(f) O2 : 1.0%
(g) O2 : 2.5%
(h) O2 : 5.0%
(i) O2 : 10.0%
Heat generation rate dQ/dt [kW/kg]
Accumulated heat generated Q [kJ/kg]
Time [min]
140 °C
200 °C
220 °C
240 °C
260 °C
300 °C

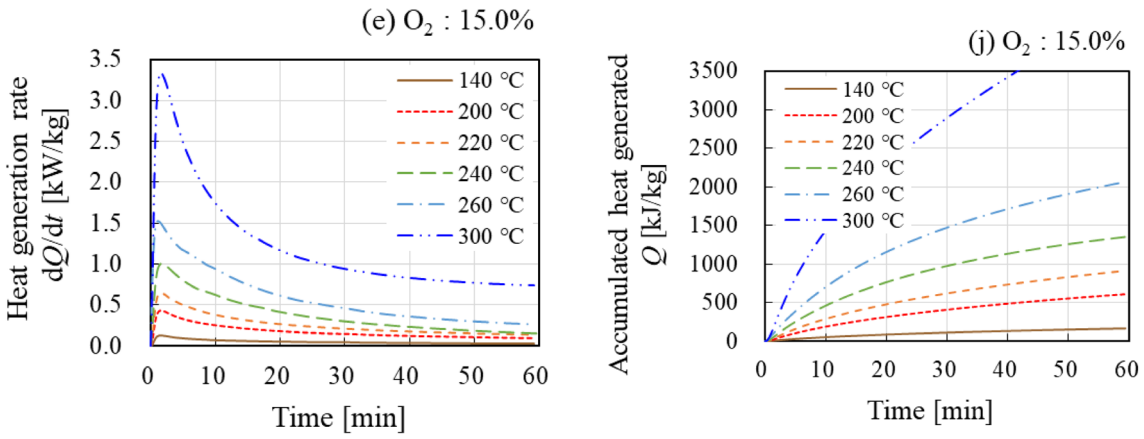


Fig. 3 Change in the heat generation rate of upgraded brown coal during oxidation treatment at different temperatures and O_2 concentrations.

value increased with higher O_2 concentrations and oxidation treatment temperatures, indicating that these factors influence the rate of the oxidation reaction.

3.2 Evaluation of the heat generation of oxidation-treated upgraded coal

Fig. 4 illustrates the heat generated when the oxidized upgraded coal was exposed to dry air (21 vol% O_2) at 107 °C. For comparison, the heat generated by the upgraded brown coal without oxidation treatment and bituminous coal dried in N_2 atmosphere is also presented.

The oxidation treatment significantly reduced the heat generation of the upgraded brown coal, regardless of the oxidation treatment conditions. Specifically, oxidation treatments at 200 °C with O_2 concentrations of 5 vol% or higher, and at 240–260 °C with O_2 concentrations of 2.5 vol% or more, resulted in heat generation from the upgraded brown coal that was equal to or lower than that of bituminous coal during the 60-min oxidation period. Additionally, treatments at 240 °C and 260 °C similarly reduced heat generation across all O_2 concentrations. From an industrial perspective, a reduction in yield due to oxidation treatment is undesirable. Given that the yield decreased above the oxidation temperature of 260 °C (**Fig. 2**), 240 °C is the optimal temperature for the oxidation treatment of the upgraded brown coal.

3.3 Evaluation of the oxidation reaction rate

Fig. 5 shows plots of the weight change at the end point of the oxidation treatment (60 min) versus the accumulated heat generation, using the data from **Figs. 2** and **3**. Evidently, the correlation between weight change and accumulated heat generation was almost monotonous for samples oxidized for temperatures below 240 °C. Conversely, for the oxidation treatment above 260 °C, the weight of the coal decreased while generating intense heat, resulting in a different correlation between weight and heat value compared to the range up to 240 °C. These findings suggest that reactions such as oxygen adsorption and the formation of peroxides and carboxyl groups primarily occur up to 240 °C, while gasification of the functional groups begins above 260 °C.

As discussed in Section 3.2, temperatures of 240 °C or lower are optimal for oxidation treatment when considering the yield. Furthermore, while the oxidation reaction of coal involves multiple reactions, it can be represented by a formula assuming it follows a zero-order or first-order reaction with respect to the unreacted coal rate [20, 21], or by Elovich's equation (an empirical equation describing the rate of gas adsorption on a solid surface) [22]. Therefore, the weight change during the oxidation treatment up to 240 °C was assumed to follow a general oxidation reaction (apparent first-order reaction) owing to the introduction of oxygen into the coal, as expressed in Eq. 1, and the reaction rate was assessed:

$$\text{Coal} + \text{O}_2 \xrightarrow{k} \text{Oxidized coal} \quad \cdots\cdots (1)$$

In Eq. 1, k represents the reaction rate constant derived from the Arrhenius plot. It was assumed that, after the reaction with O_2, the coal's weight increased, resulting in oxidation-treated coal. While a reaction route, wherein CO and CO_2 are gasified during oxidation treatment, exists, the weight change reportedly reaches a saturation point, and gas generation stabilizes at oxidation treatment temperatures up to 240 °C [19]. Therefore, assuming that a certain amount of gas is generated in proportion to the weight increase rate and that neglecting this effect does not influence the superiority of the weight change trend for each oxidation treatment condition, the effect of gasification of the functional groups was disregarded. The results in **Fig. 4** indicate that the upgraded coals subjected to a 60 min oxidation treatment at 200 °C with an O_2 concentration of 5.0 vol% generated almost the same amount of heat as the bituminous coal; consequently, the weight increase at this point was used as the reference (the weight increase corresponding to the desired heat generation level) to define the reaction end point. The reaction rate constant was then estimated based on the time required for the weight to reach this value under other oxidation treatment conditions.

Fig. 6 depicts the Arrhenius plot for the oxidation reaction of the upgraded coal. At 140 °C and 1.0 vol%-O_2, the target weight was

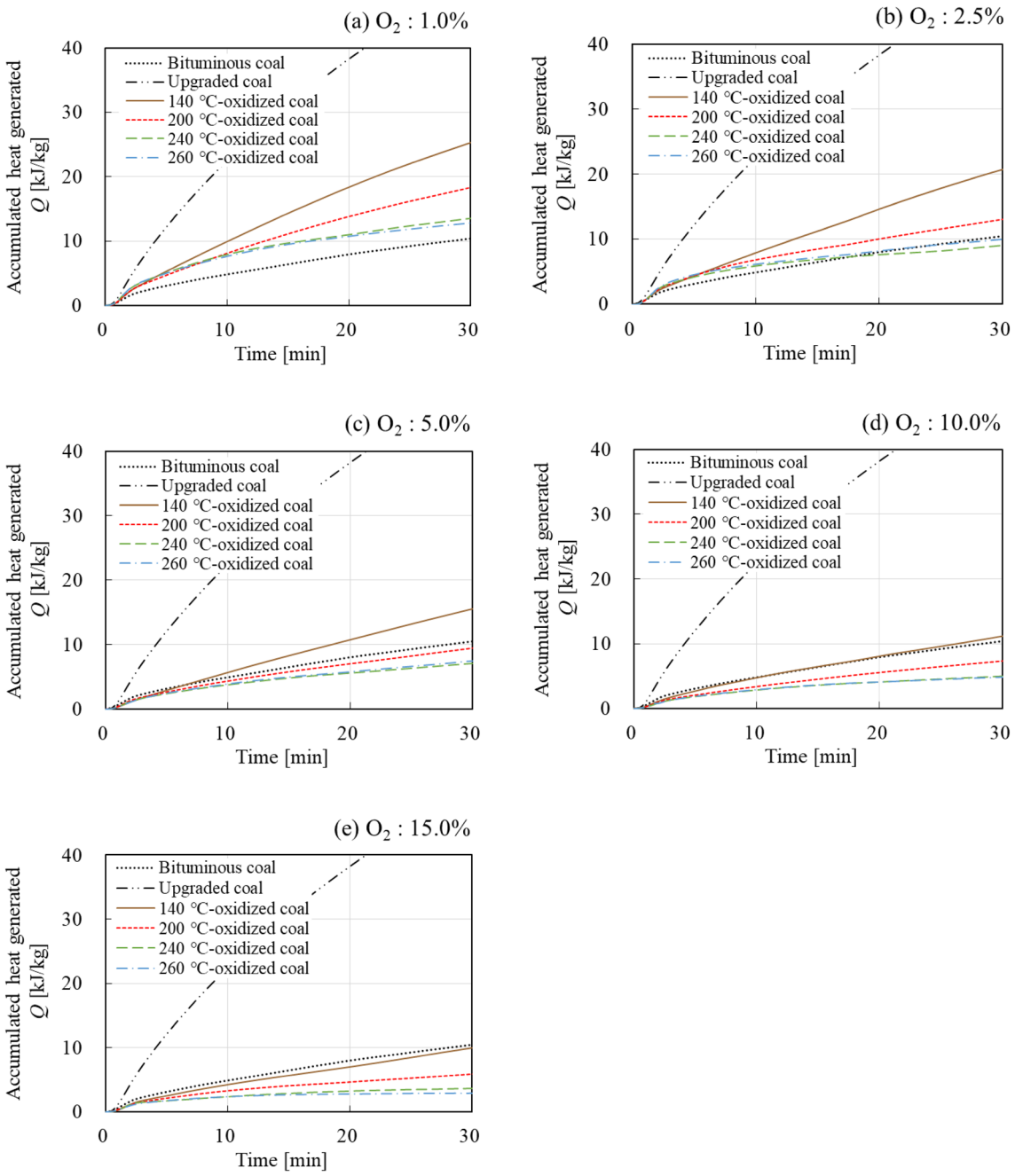


Fig. 4 Change in the heat generation rate of upgraded brown coals oxidized at different temperatures and O_2 concentrations during reaction with dry air.

not reached within the 60-min treatment period, and therefore, the *k* values could not be determined. Likewise, for 2.5 vol%-O_2, no results were obtained at 200 °C and 220 °C within 60 min, so only the point at 240 °C, where results were obtained, is presented. Thus, the results for samples treated at 200–240 °C with O_2 concentrations of 5–15 vol% are depicted in **Fig. 6**.

The activation energy, E_a, calculated from the Arrhenius equation, was approximately 60 kJ/mol, independent of the O_2 concentration. This value is close to the reported activation energy for the air oxidation of coal, ranging from brown coal to bituminous coal, within the tested temperature range [21]. Conversely, the O_2 concentration appeared to correlate with the frequency factor *A*: **Fig. 7** presents a plot of the frequency factor versus the O_2 partial pressure, P_{O2}.

To derive an estimation equation for the oxidation rate of the upgraded brown coal under reaction conditions of 200–240 °C and 5–15 vol%-O_2, incorporating the factor of P_{O2}, an Arrhenius-type equation, as shown in Eq. 2, was proposed. Here, *a* and *b* are constants, *T* represents the oxidation temperature, and *R* denotes the gas constant. The parameters are listed in **Table 2**. The constants *a* and *b* were determined from the approximation formula of the frequency factor *A* and the P_{O2} in **Fig. 7**. The activation energy E_a was calculated as the average of the results at O_2 concentrations of 5, 10, and 15 vol%:

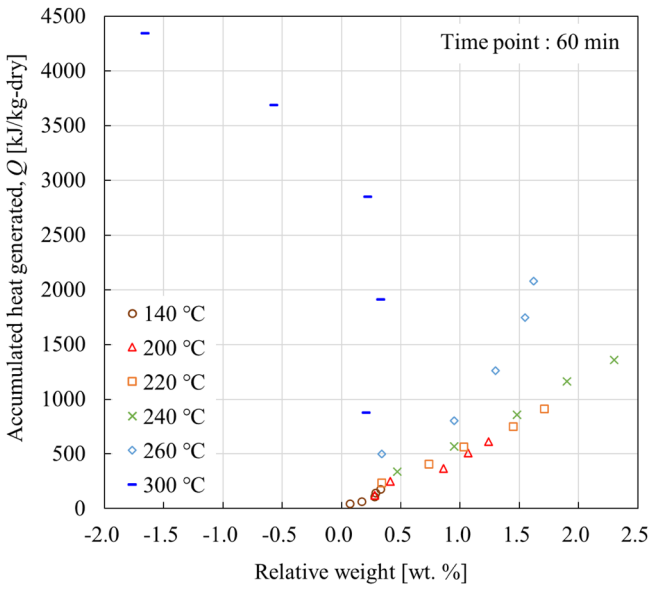


Fig. 5 Correlation of the relative weight and accumulated heat generation, Q, of the upgraded brown coals oxidized at different temperatures and O_2 concentrations through the reaction with dry air.

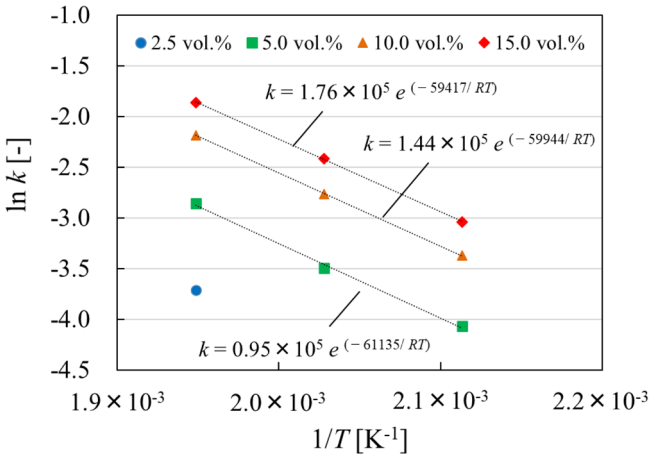


Fig. 6 Arrhenius plots of the reaction rate constant, k.

$$\ln k = a + b\ln(P_{O2}) - E_a / RT \quad \cdots\cdots (2)$$

By applying Eq. 2, the treatment time needed for the upgraded brown coal to reach a heat release rate equivalent to that of bituminous coal can be determined based on the O_2 partial pressure and treatment temperature. For instance, it was found that oxidation treatment at 240 °C takes about one-third of the time required for treatment at 200 °C. Additionally, increasing the oxidation treatment temperature proves to be more effective in reducing treatment time than increasing the O_2 partial pressure.

4. Conclusion

This study demonstrates that the oxidation treatment of upgraded Australian brown coal effectively reduced spontaneous heating to levels similar to that of bituminous coal. Oxidation treatment temperatures of 240 °C or lower were adequate, while temperatures above 260 °C led to a decrease in yield, with spontaneous heating suppression comparable to that achieved at 240 °C. Furthermore, the reaction rate for oxidation at temperatures up to 240 °C was formulated. The apparent activation energy was found to be approximately 60 kJ/mol, and a strong correlation was observed between the O_2 concentration during oxidation and the frequency factor. An estimation equation was developed to predict the oxidation conditions of the upgraded brown coal.

This research is expected to help broaden the range of coal resource options. In the future, we plan to assess the oxidation treatment and the effects of ignition suppression using larger sample sizes to validate the effectiveness of the proposed equation.

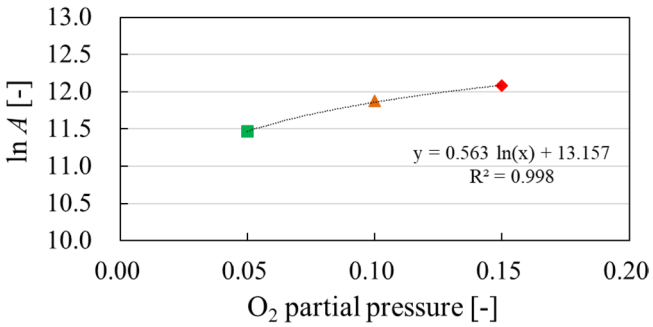


Fig. 7 Correlation of O_2 partial pressure and the frequency factor, A.

Table 2 Reaction rate parameters.

a [-]	b [-]	E_a [kJ/mol]
13.157	0.563	60.1

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