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Suppression of the spontaneous combustion of upgraded brown coal

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Brown coal is characterized by a high moisture and volatile matter content, but its heating value per unit weight is low. To use it as a substitute fuel for bituminous coal, it must be dried and carbonized to increase its heating value to a level comparable to that of the bituminous variety. During this upgrading process, careful consideration must be given to its combustion efficiency while retaining a certain proportion of volatile matter. However, the upgraded coal containing volatile matter poses a considerable risk of spontaneous combustion, preventing long-distance transportation and long-term storage. This study proposes a straightforward method to suppress this spontaneous combustion by stabilizing the aliphatic hydrocarbons. Quantum chemical calculations have shown that the carboxyl and ester groups produced during the oxidation of methyl groups in the upgraded coal have a high chemical stability. Based on these results, Loy Yang coal, a representative brown coal from Victoria, Australia, was upgraded at 430 °C, and its oxidative behavior was evaluated using FT-IR, nuclear magnetic resonance, thermogravimetry/differential thermal analysis, and gas chromatography. The results confirmed that oxidizing the upgraded coal at 240 °C effectively reduced its tendency for spontaneous combustion.

KEYWORDS : Brown coal, Oxidation treatment, Quantum chemical calculations, Spontaneous combustion, Upgraded coal

1. Introduction

Coal remains a crucial energy resource owing to its widespread availability and relatively stable pricing. It serves as a foundational power source, requiring the procurement of reliable and affordable coal to ensure the stability of coal-fired power generation. However, in recent years, increasing demand in coal-producing nations and geopolitical tensions have strained the supply-demand equilibrium, leading to surging prices and challenges in securing stable coal supplies. Moreover, coal-fired power generation hit record highs between 2021–2023, with China, India, and Southeast Asia setting new records [1, 2]. In contrast, biomass-derived feedstock's have attracted attention in recent years; however, they present challenges related to supply capacity in meeting electricity demand and the high costs of constructing biomass power generation facilities [3]. Consequently, until advancements are made in carbon capture, utilization, and storage technologies, coal will continue to be a primary feedstock both domestically and internationally. Therefore, upgrading and stably using low-rank coal, which is currently underused but abundant in reserves, are being considered as alternatives to thermal coal for power generation from a medium- to long-term perspective [4].

Low-rank coal is characterized by high moisture and volatile matter content, and its heating value per unit weight is low. The high moisture content of low-rank coal compromises its transportation efficiency, limiting its usage primarily to areas near coal-producing regions unless it undergoes drying or reforming [5]. During the drying and reforming processes, it is crucial to upgrade the coal while ensuring that a certain amount of volatile matter is retained to prevent a decline in combustion efficiency (combustibility). In this context, "upgrading" pertains to a process of dry distillation applied to coal at low to medium temperatures. This process removes volatile components and increases calorific value. However, the upgraded coal retains some volatile matter, which makes it highly susceptible to spontaneous combustion, hindering its suitability for transportation and storage. Thus, the primary goal of this study was to develop methods to suppress the spontaneous combustion of low-rank coal, even after

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undergoing the upgrading process.

Fig. 1 shows a structural model for German brown coal, as proposed by Hüttinger [6]. This model depicts brown coal as having a molecular structure primarily composed of mono- to tri-cyclic aromatic rings, with aliphatic hydrocarbons such as methyl groups ($-CH_3$) and oxygen-containing functional groups such as carboxyl groups ($-COOH$) attached to the molecular backbone. It is believed that coal undergoes ignition owing to the heat generated by moisture adsorption [7, 8] and by oxidation reactions involving functional groups, which convert aliphatic hydrocarbons into oxygen-containing functional groups [9–14] that ultimately decompose into CO, CO_2, and H_2O.

Fig. 2 shows an exothermic oxidation reaction scheme for coal, as proposed by Miura *et al.* [14]. This scheme suggests that between 140 °C and 320 °C, aliphatic hydrocarbons ($-CH_3$) undergo a series of oxidation reactions. At temperatures of 320 °C and above, the functional groups decomposes into CO, CO_2, and H_2O. Because these reactions are exothermic, the spontaneous combustion of coal can be attributed primarily to oxidation reactions involving aliphatic hydrocarbons and oxygen-containing functional groups, as depicted in **Fig. 2**.

Assuming that the spontaneous combustion of upgraded charcoal is also caused by the oxidation of functional groups, we hypothesized that stabilizing these functional groups could mitigate spontaneous heat generation and ignition during storage and transportation. Therefore, we implemented a three-step approach: (1) we used quantum chemical calculations to identify chemically stable functional groups; (2) we performed controlled oxidation treatments of the functional groups in upgraded coal to transform them into the stable state predicted by the quantum chemical calculations; and (3) we evaluated the oxidized upgraded coal with stabilized functional groups for their efficacy in suppressing spontaneous combustion.

2. Experimental

2.1 Prediction of chemically stable functional groups

Assuming that the oxidation reactions of upgraded coal follow the scheme outlined in **Fig. 2**, we used quantum chemical calculations to identify energetically stable functional groups. These calculations were performed using the B3LYP method, a density-functional theory approach, to determine the energy levels of stable structures during structural optimization. The Gaussian 09 program was used for these calculations, and the 6-31G* basis set was employed. As a simplified model for low-rank coal, we used a toluene molecule structure, which consists of a methyl group attached to a monocyclic aromatic ring. This structure served as the starting molecule for the reaction.

2.2 Changes in functional groups by oxidation reactions

Loy Yang coal, a typical Australian brown coal, was crushed to 1–3 mm and carbonized at 430 °C for 60 min in a horizontal tube furnace, yielding upgraded coal with 25 wt% volatile matter.

For the oxidation treatment, 10 g of the prepared upgraded coal

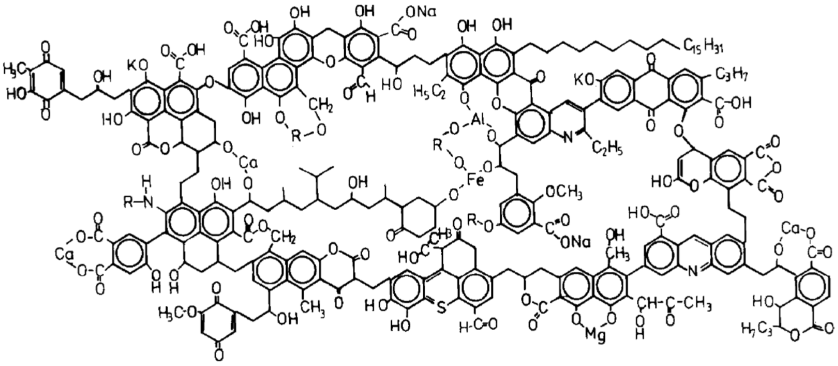

Fig. 1 Proposed structural model for brown coal [6] (Reprinted from Fuel, 66(8), K. J. Hüttinger, A. W. Michenfelder, Molecular structure of a brown coal, 1164–1165. Copyright (1987), with permission from Elsevier).

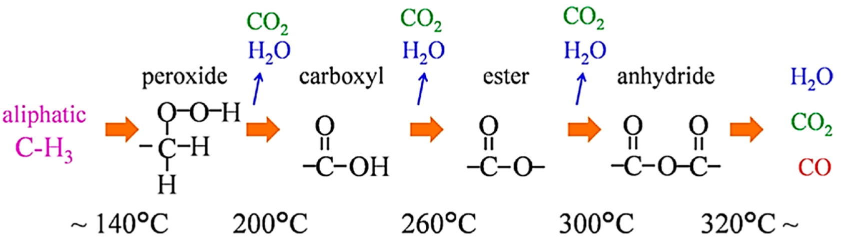

Fig. 2 Proposed scheme of functional group changes in coal owing to oxidation reactions [14] (Reprinted with permission {H. Fujitsuka, R. Ashida, M. Kawase, K. Miura, Examination of low-temperature oxidation of low-rank coals, aiming at understanding their self-ignition Tendency, Energy & Fuels, 2014, 28(4): 2402–2407}. Copyright (2014) American Chemical Society).

was placed in a tube furnace, and N_2 was introduced at a flow rate of 200 mL/min. Then, the temperature was increased to 200 °C, 240 °C, 260 °C, or 300 °C at a heating rate of 10 °C/min. Next, the N_2 was replaced with a mixed gas of O_2 and N_2 (O_2 concentration: 2, 4, or 8 vol%). Oxidation treatment was then performed for 45 min. Subsequently, the mixed gas was switched back to N_2, and the furnace was cooled to room temperature under an N_2 atmosphere. The oxidized upgraded coal was then collected.

Fourier-transform infrared (FT-IR) spectroscopy (JASCO, FT-IR 615) and ^1H nuclear magnetic resonance (NMR) spectroscopy (JEOL ECA-400) were used to analyze the types and quantities of functional groups in the upgraded and oxidized coal. For FT-IR measurements, the samples were prepared using the KBr pellet method.

2.3 Weight change and gas generation during oxidation treatment

The weight-change trends and heat-generation characteristics during the oxidation treatment of upgraded coal were analyzed using thermogravimetric and differential thermal analysis (TG/DTA). First, the upgraded coal, prepared as described in Section 2.2, was crushed to a particle size below 212 µm and then loaded into the instrument. After reaching the desired oxidation treatment temperature (ranging from 140 °C to 300 °C) at a heating rate of 10 °C/min under N_2, the atmosphere was switched to a gas mixture containing 8 vol% O_2. The weight changes were then recorded while maintaining the target temperature for 120 min. The gas exiting the tube furnace was collected in a gas bag and analyzed using a gas chromatograph equipped with a thermal conductivity detector (GC-TCD) to quantify CO_2 gas generated. The gas flow rate during the oxidation treatment was maintained at 100 mL/min, and the generated gas was collected every 20 min at each temperature.

2.4 Gas diffusivity in particles during oxidation treatment

Upgraded coal particles with diameters ranging from 3 to 4 mm were prepared and oxidized at a temperature of 200 °C in an O_2 atmosphere with concentrations of 2, 4, or 8 vol%. Oxidation treatment times of 40, 80, or 160 min were used. The atomic number ratio of oxygen atoms to carbon atoms (O/C) on the surface and in the interior of upgraded coal particles, both before and after oxidation treatment, was determined using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX, JEOL-JCM6000). To determine the O/C ratio in the coal particles, the oxidized samples were ground to a size below 212 µm to expose their interiors. The O/C ratio of the exposed particle cross-sections was then measured using SEM-EDX. It should be noted that only carbon and oxygen were detected by SEM-EDX, and the ratio of their elemental contents was defined as O/C. These measurements were performed with $n=10$, and the average values were calculated as the measurement data.

2.5 Suppression of spontaneous combustion in oxidized coal

A 10-g sample of upgraded coal was oxidized for 40 min in a horizontal tube furnace at temperatures of 200 °C and 240 °C under a flow of 8 vol% O_2 (N_2 base) at a flow rate of 200 mL/min. To assess the ignitability of the upgraded coals before and after oxidation treatment, their ignition points were measured using an ignition point measuring apparatus following the JIS K1474 standard. A 10 mL sample of upgraded coal was loaded into a dedicated container and heated at a rate of 10 °C/min under a flow of dry air at a rate of 500 mL/min. When the sample began to self-heat and ignite, a rapid increase in temperature was observed. A temperature rise trend graph was constructed with time on the horizontal axis and temperature on the vertical axis. The ignition point was defined as the intersection of tangent lines drawn along the slopes of the curves before and after the rapid temperature increase.

3. Results and Discussion

3.1 Examination of chemically stable functional groups

Fig. 3 shows the optimized structures and calculated energy levels of various functional groups, as determined through quantum chemical calculations. The energy levels were calculated based on the assumption that oxidation begins with the methyl group, progressing through an aliphatic hydrocarbon of methyl ($-CH_3$) to peroxide ($-CH_2OOH$), aldehyde ($-CHO$), carboxyl ($-COOH$), ester ($-COOR$), and finally to an anhydride group ($-COOCOR$), following the oxidation reaction pathway depicted in **Fig. 2**.

The energy level of a reaction can be determined by comparing the energies of the reactant and each product. If the energy level of the product is higher than that of the reactant, the reaction is endothermic; otherwise, it is exothermic. The quantum chemical calculations

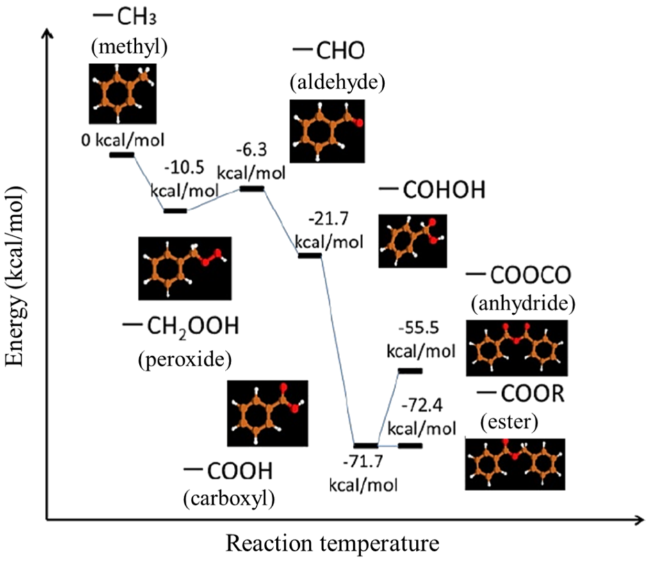

Fig. 3 Energy changes of functional groups during oxidation reactions.

corroborated the validity of the oxidation reaction pathway presented in **Fig. 2**, indicating its involvement in spontaneous heat generation. Notably, the calculations revealed a substantial exothermic reaction coinciding with the formation of a carboxyl group, suggesting that carboxyl and ester groups are the most stable reaction products. While the conversion of methyl to peroxide is exothermic, the subsequent conversion from peroxide to aldehyde is endothermic. Nonetheless, the energy difference between peroxide and aldehyde is minimal, and the oxidation reaction from aldehyde to carboxyl is highly exothermic, as previously mentioned. Consequently, it is plausible that during the oxidation of methyl, it may not stabilize as peroxide but rather rapidly proceed to form carboxyl. Furthermore, the conversion of carboxyl to anhydride during further oxidation is an endothermic reaction, rendering it less stable. Considering these results and **Fig. 2**, we propose that the optimal oxidation treatment temperature for reformed carbon should be in the range of 200–300 °C. At these temperatures, the methyl, peroxide, and aldehyde groups present in reformed carbon can be converted to carboxyl groups, resulting in the most stable functional group configuration. Conversely, if oxidation treatment is performed at temperatures exceeding 300 °C, the carboxyl groups will undergo further conversion to anhydrides, leading to chemical instability. Consequently, we conclude that the optimal oxidation treatment temperature range is 200–300 °C.

3.2 Changes in functional groups during oxidation reaction

Table 1 presents the results of proximate, ultimate, and heating value analyses performed on raw brown coal, the upgraded coal, and the oxidized upgraded coals used in this study. Additionally, the weight change observed before and after oxidation treatment is reported. It is important to note that the oxygen content was directly measured rather than calculated by difference. For comparative purposes, the results obtained for a sub-bituminous coal A and a bituminous coal B are also included. As evident from **Table 1**, the upgraded coal had a lower yield of volatile matter owing to the carbonization process, which in turn increased the carbon content ratio and resulted in a higher heating value equivalent to that of bituminous coal B. Conversely, the oxidation treatment applied to the upgraded coal led to an increase in the oxygen content ratio and a decrease in the heating value. Notably, the oxidation treatment performed at 200 °C resulted in weight gain, whereas that performed at 300 °C caused weight loss. Based on these observations and the results of the ultimate analysis, we can infer that the primary reaction occurring at 200 °C was weight gain owing to oxygen incorporation, while at 300 °C, the dominant reaction was weight loss resulting from the partial gasification of carbon and hydrogen species.

Fig. 4 shows the FT-IR spectra of oxidized upgraded coal treated at temperatures of 200 °C or 300 °C with an O_2 concentration of 8 vol%. Each spectrum was normalized using the peak height of aromatic carbon (1620 cm^{-1}), which is assumed to remain unaffected by oxidation treatment in this temperature range. As evident from **Fig. 4**, a peak corresponding to the carboxyl group appeared near 1700 cm^{-1} after oxidation treatment at 200 °C. Conversely, following oxidation treatment at 300 °C, the intensity of the carboxyl group peak decreased, while peaks corresponding to the ester and anhydride groups appeared at 1770 and 1740 cm^{-1}, respectively. In contrast, for aliphatic hydrocarbons, the peak intensities at approximately 2850 and 2920 cm^{-1} decreased, indicating their consumption owing to the oxidation reaction.

To further elucidate the consumption trend of aliphatic hydrocarbons during oxidation treatment, we used ^{1}H-NMR spectroscopy to assess the reduction in aliphatic hydrocarbon content. **Fig. 5** shows the ^{1}H-NMR spectra of oxidized upgraded coals treated at temperatures ranging from 200 °C to 300 °C in an 8 vol% O_2 atmosphere. The spectra indicate a tendency for the amount of aliphatic hydrocarbons to decrease with increasing oxidation treatment temperature.

Table 1 Compositions of brown coal-derived samples used in this study.

Coal		Oxidation treatment conditions		Ultimate analysis [wt%, dry]					Proximate analysis [wt%, dry]			Ratio of weight variation [%]	Higher heating value [kcal/kg]
		Oxygen concentration [%]	Treatment temperature [°C]	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	—	—	77.0	3.6	0.8	15.0	0.3	3.4	24.6	72.0	Base	7170
	Oxidized coal	2.2	200	75.3	3.3	0.8	15.3	0.3	3.4	26.8	69.9	0.2	6914
			300	74.8	3.3	0.7	15.4	0.3	3.8	25.9	70.3	−0.9	6893
		3.7	200	74.0	3.2	0.8	16.8	0.3	3.2	27.4	69.3	0.9	6814
			300	73.3	3.1	0.8	17.4	0.3	3.8	27.5	68.7	−1.3	6735
		7.9	200	73.1	3.1	0.8	17.8	0.3	3.2	29.0	67.8	1.4	6706
			300	71.1	2.9	0.8	20.1	0.3	3.4	30.1	66.5	−4.2	6446
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

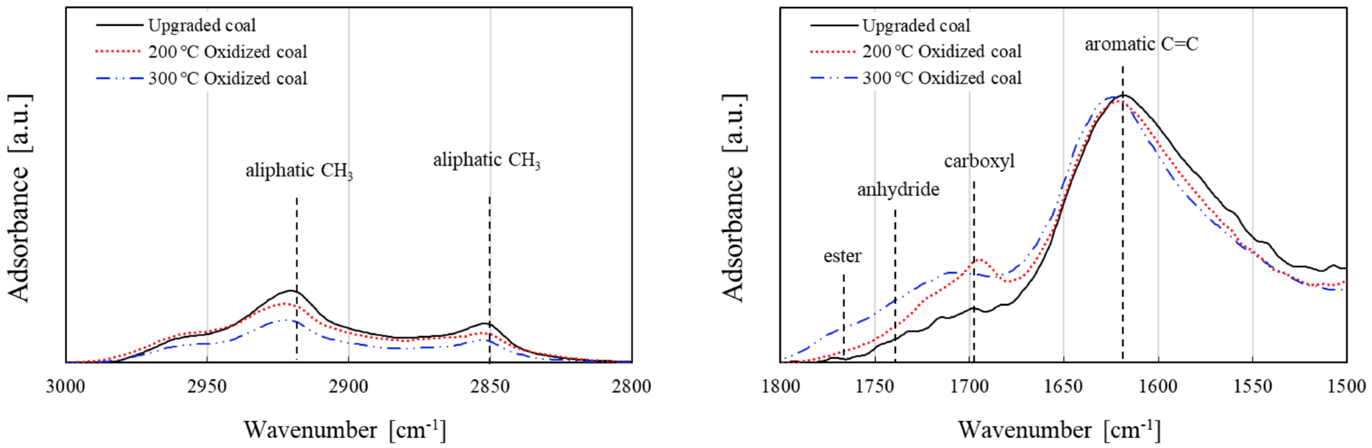

Fig. 4 FT-IR spectra of upgraded brown coal before and after oxidation treatment.

Table 1 shows that as the temperature increases from 200 °C to 300 °C, the carbon content decreases while the oxygen content increases. This suggests the oxidation of aliphatic hydrocarbons. The quantum chemical calculation results presented in **Fig. 3** suggest that during the oxidation of aliphatic hydrocarbons, the reaction proceeds rapidly to form carboxyl groups. Moreover, the FT-IR results shown in **Fig. 4** indicate that carboxyl groups are indeed formed at temperatures as low as 200 °C. Based on these observations, we infer that oxygen is incorporated into aliphatic hydrocarbons, leading to the formation of carboxyl groups during oxidation treatment up to 200 °C. However, at 300 °C, a decrease in weight was observed, and the peak corresponding to carboxyl groups in **Fig. 4** shifted to ester and anhydride groups. This suggests that the carboxyl groups formed at 200 °C undergo further oxidation to form esters and anhydrides, while some are gasified as CO and CO_2. These observed reaction trends align with the oxidative reaction scheme of functional groups in raw coals depicted in **Fig. 2**, suggesting that the oxidation reaction of aliphatic hydrocarbons in the upgraded coals follows a similar pathway. It is important to note that while O_2 concentration was not used as a parameter in the FT-IR and ^{1}H-NMR measurements in this study, it is reasonable to assume that O_2 concentration influences the extent of reaction per unit treatment time, in other words, the reaction rate. Therefore, it can be inferred that the oxidation reaction processes of aliphatic hydrocarbons remain essentially unchanged even under varying O_2 concentrations.

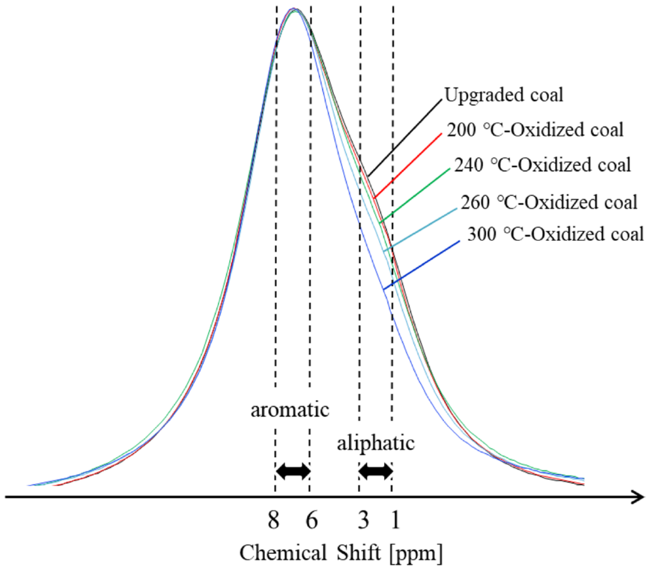

Fig. 5 ^{1}H-NMR spectra of upgraded brown coal before and after oxidation treatment.

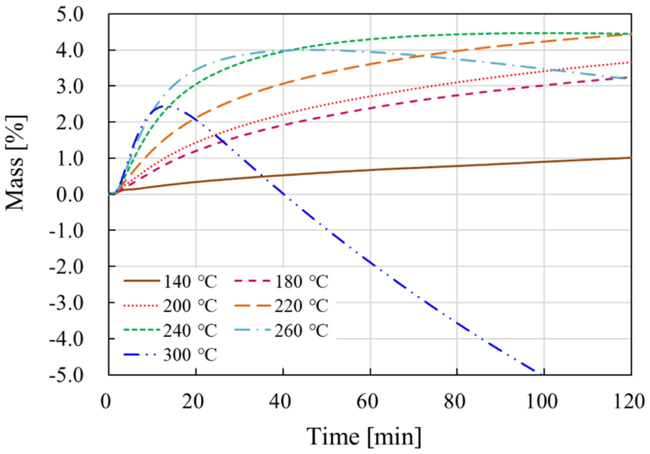

Fig. 6 Weight change of upgraded brown coal during oxidation treatment at different temperatures.

3.3 Weight change and gas generation during oxidation treatment

Figs. 6 and **7** show the TG/DTA results obtained during the oxidation treatment of upgraded coal. **Fig. 6** demonstrates that an immediate weight increase occurs upon the commencement of oxidation treatment at all temperatures examined. This is attributed to the incorporation of oxygen into the functional groups. Notably, when the oxidation treatment temperature reaches 260 °C or higher, the initial weight gain is followed by a weight decrease. Furthermore, **Fig. 7** shows that the weight increase observed during oxidation treatment is exothermic, and occurs transiently in a time frame ranging from several min to several tens of min after the initiation of oxidation treatment.

Fig. 8 shows the quantities of CO and CO_2 produced during the oxidation treatment of upgraded coal. Because the gas was collected every 20 min, the data point for 20 min, for instance, represents the average concentration of the gas collected from 0 to 20 min. As evident from **Fig. 8**, both CO and CO_2 are generated during the oxidation treatment, with the amount of CO_2 generated being approximately 2–3 times higher than that of CO. Moreover, while the quantities of CO and CO_2 generated exhibit a decreasing trend after 40 min of oxidation treatment at temperatures up to 240 °C, at temperatures of 260 °C or higher, similar or even greater amounts of these gases continue to be generated beyond the 40-min mark. Considering the weight loss trend observed in **Fig. 6**, it can be inferred that the gasification reaction of the functional groups progresses at an accelerated rate at temperatures of 260 °C or higher.

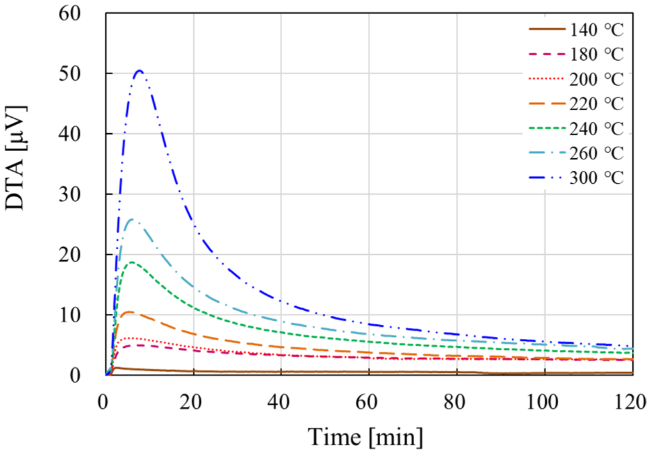

Fig. 7 Thermal generation trend of upgraded brown coal during oxidation treatment at different temperatures.

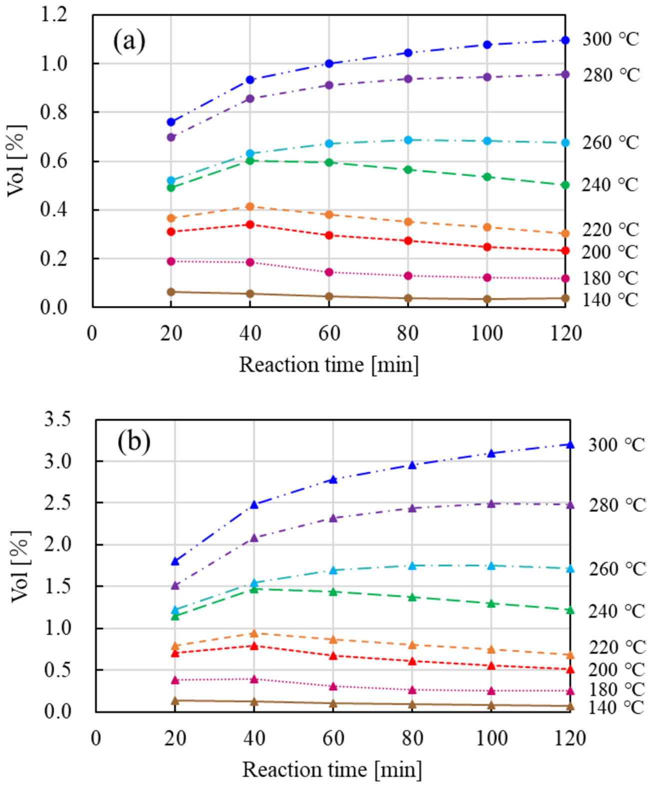

Fig. 8 (a) CO and (b) CO_2 generation during oxidation treatment of upgraded brown coal at different temperatures.

From an industrial standpoint, a shorter oxidation treatment duration is preferable; however, a reduction in yield owing to the gasification of upgraded coal is undesirable. Additionally, as indicated in **Table 1**, higher oxidation treatment temperatures lead to lower heating values. Consequently, the determination of optimal oxidation treatment conditions requires careful consideration not only of the stability of the oxidized upgraded coal but also of its yield and heating value. Conversely, the quantum chemical calculation results presented in **Fig. 3** indicate that the carboxyl group exhibits chemical stability, and **Fig. 4** shows the formation of carboxyl groups through oxidation treatment at 200 °C. Additionally, **Fig. 6** shows that the yield remained constant during oxidation treatment at temperatures of 240 °C or lower. Therefore, based on the O_2 concentration and oxidation treatment period used in this study, a treatment temperature range of 200–240 °C for oxidizing aliphatic hydrocarbons to carboxyl groups is considered the most efficient for suppressing self-heating while maintaining yield and heating value.

3.4 Gas diffusivity in particles during oxidation treatment

Figs. 9 and **10** show the oxygen content ratio after oxidation treatment, as determined by SEM-EDX. **Fig. 11** shows SEM images of the fractured cross-section of the oxidized treated carbon. These results confirm that oxidation tends to progress even at the center of the particles as the O_2 concentration is increased or the treatment time is extended. This likely occurs because the moisture content of the raw Loy Yang coal used in the analysis was approximately 60 wt%, and the volatile matter content in the upgraded coal was reduced from 50 to 25 wt% by the carbonization process. This reduction in volatile matter content renders the upgraded coal more porous, allowing O_2

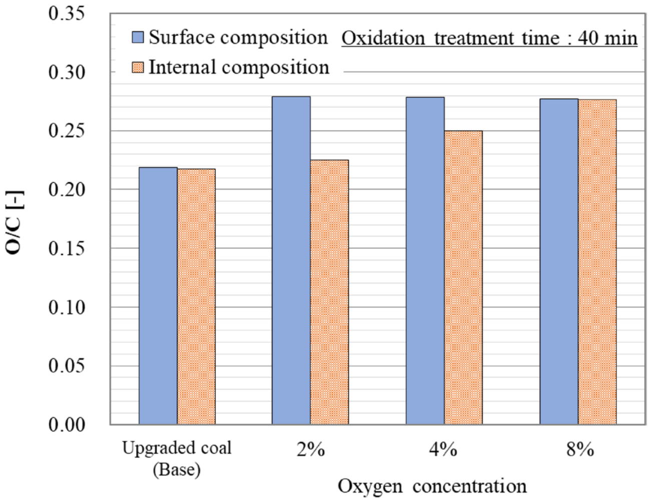

Fig. 9 Oxygen content of upgraded brown coal before and after oxidation treatment at 200 °C for 40 min under different O_2 concentrations.

molecules to diffuse into the interior of the particles. Indeed, micrometer-scale pores were observed, as shown in **Fig. 11**.

Notably, there is no discernible difference in the oxygen content ratio between the surface and interior of the oxidized upgraded coal that underwent oxidation at an O_2 concentration of 8 vol% for 40 min. This observation suggests that even the interior of the particles is adequately oxidized. Furthermore, **Figs. 9** and **10** show that the total amount of O_2 molecules supplied was increased at the same rate, and comparable oxygen content ratios were achieved in the resulting oxidized coals even when different parameters (O_2 concentration and time) were varied. This indicates that the O_2 supply may be the rate-determining factor in the oxidation reaction of the upgraded coal. Therefore, it is reasonable to assume that if the amount of O_2 supplied per unit of upgraded coal during the oxidation treatment is increased, the oxidation process can be completed in a shorter time (or in a similar time for larger particle sizes). However, it is important to note that because the oxidation process is exothermic, it is necessary to promote heat dissipation or heat extraction to achieve rapid oxidation treatment. While this study used a fixed bed system, in an actual industrial process, it would be advantageous to use equipment such as a fluidized bed that can uniformly and efficiently extract heat from the entire volume of upgraded coal. This could be achieved, for example, by continuously supplying a sufficient volume of combustion exhaust gas (O_2 concentration of 5–10 vol%) of approximately 200 °C against the upgraded coal and extracting the heat generated by the oxidation treatment through the combustion exhaust gas.

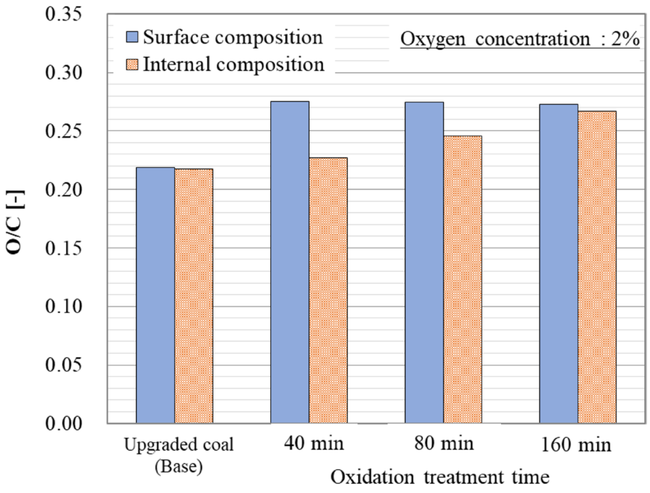

Fig. 10 Oxygen content of upgraded brown coal before and after oxidation treatment at 200 °C with 2 vol% O_2 for different treatment times.

3.5 Suppression of spontaneous combustion in oxidized coal

Fig. 12 shows the ignition point measurement results obtained before and after the oxidation treatment. The ignition point of a sample of raw Loy Yang coal dried at 107 °C for 3 h was 208 °C, while the upgraded coal after carbonization to 25 wt% volatile matter content exhibited increased ignitability, with the ignition point decreasing to 194 °C. This observation can be attributed to the presence of dangling bonds that remain in a chemically unstable state after the volatile matter is removed by the carbonization process. Additionally, the increase in surface area resulting from the upgrade (removal of volatile components) may have led to an increase in the reaction surface, thereby enhancing the amount of oxidation reaction per unit time.

In contrast, the ignition point of the oxidized upgraded coal treated at 200 °C was 238 °C, which is higher than that of the upgraded coal. The oxidized upgraded coal treated at 240 °C exhibited an even higher ignition point of 258 °C. Both oxidized upgraded coal samples had ignition points that exceeded that of bituminous coal B, which serves as a benchmark. This indicates that oxidation treatment at 200–240 °C can effectively stabilize the functional groups of upgraded coal and increase its ignition point to a level comparable to that of thermal coal.

We believe that the findings of this study contribute to broadening the range of viable coal resources. Furthermore, the increased use of biomass-derived feedstocks, such as wood pellets, represents a step toward achieving a decarbonized society. Torrefaction has been demonstrated to be an effective technique for wood pellet production, leading to improvements in friability, ignitability, and heating value [15–17]. However, it is recognized that heat-treatment methods, including drying and torrefaction, can enhance spontaneous combustibility, similar to what is observed in coal [15, 18]. Biomass feedstocks are also abundant in aliphatic hydrocarbons and oxygen-

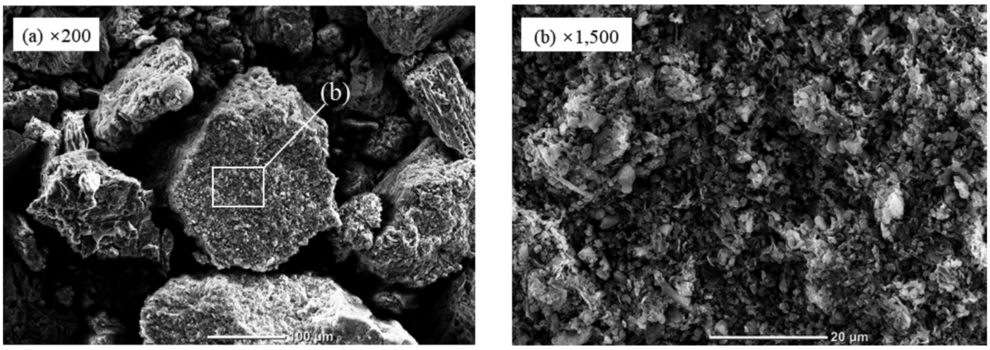

Fig. 11 SEM images of oxidized coal (200 °C, 8 vol% O_2, 40 min).

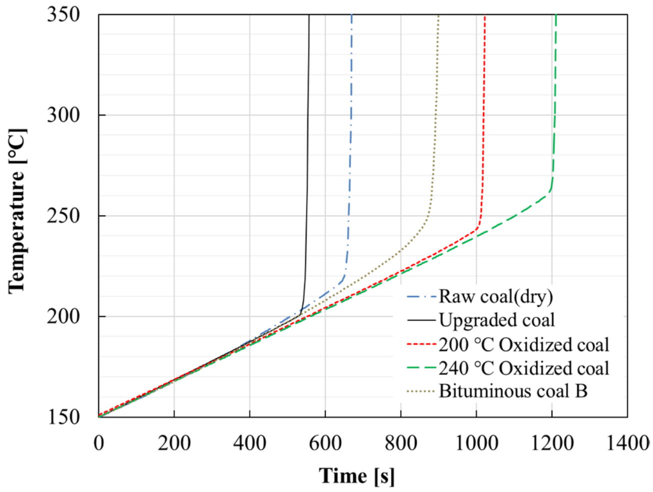

Fig. 12 Change in flammability of upgraded coal owing to oxidation treatment.

containing functional groups; therefore, it is reasonable to consider that the findings of this study can be applied to these feedstocks.

4. Conclusion

By upgrading brown coal, its heating value can be enhanced to match that of bituminous coal. Our research revealed that aliphatic hydrocarbon groups remained in the upgraded coal and contributed to heat generation during oxidation reactions. To mitigate the risk of spontaneous combustion in upgraded brown coal, we performed experimental trials to convert the aliphatic hydrocarbon groups into chemically more stable carboxyl and ester groups based on the results of quantum chemical calculations.

The upgraded coal exhibited high ignitability, with an ignition point of 194 °C. However, oxidation treatment performed at temperatures ranging from 200 °C to 240 °C, with the aim of selectively oxidizing aliphatic hydrocarbon groups to carboxyl groups, resulted in reduced ignitability, increasing the ignition point to between 238 °C and 258 °C. Notably, this ignition point was higher than that of the bituminous coal used for comparison. We also confirmed that in the temperature range of 200–240 °C, the functional groups underwent minimal gasification, effectively suppressing yield loss associated with the oxidation treatment. Additionally, our findings suggest the possibility of oxidative stabilization of larger particle sizes, provided that sufficient O_2 is supplied. These results demonstrate the effectiveness of oxidation treatment in mitigating the ignitability of upgraded brown coal on an industrial scale.

Acknowledgements

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