Low-Temperature Oxidation Reactivity of Low-Rank Coals and Their Petrographic Properties

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ABSTRACT: Through the oxidation of coal at low temperatures and the resulting petrographic analysis, this study aims to predict spontaneous combustion, which has emerged as an industrial problem. Low-temperature oxidation analysis and the corresponding petrographic characteristics of four different coals treated under low temperatures of 25, 50, and 75 °C, which was set as the reactor temperature, were investigated. Low-temperature oxidation experiments designed at Pusan National University, based on papers related to low-temperature experiments, were conducted to analyze the constant of oxidation reactions. The petrographic characteristics of the coals were analyzed using a coal petrographic microscope spectrophotometer for determining their vitrinite reflectance and morphology, and the coals were extracted after the low-temperature oxidation experiments. After these analyses, vitrinite reflectance changed, and the normalized k, which is the difference between the constant of reaction from 25 °C to (the setting temperatures of) 50 and 75 °C, was also calculated. By comparing the oxidation rates of the coals and the corresponding petrographic analyses, the cause of spontaneous combustion can be deduced and a prediction can be made about which coal burns most efficiently at a low temperature.

1. INTRODUCTION

Most mining accidents in the recent past have been due to equipment or vehicle failure or human error despite significant advances in our understanding of spontaneous combustion in coal. In Ukraine, over 30 miners were killed in an explosion in 2014.1 Thus, spontaneous combustion is still an important safety issue within the coal industry in both coal mines and power plants.1-3 Various ranks of coal are used to generate electricity in coal power plants. Before coal is combusted in a boiler, it is first piled outdoors and/or indoors. During piling, there is a great risk of spontaneous combustion; understanding why this occurs can prevent losses and reduce the probability of further accidents.

The causes of spontaneous combustion of coal can be both physical and chemical. The height and angle of coal stockpile and how much air flows into it, along with the humidity and temperature of the surrounding environment, all affect spontaneous combustion. As for the internal causes, the physical and chemical characteristics of coal such as coal rank, coal properties (moisture, volatile matter, fixed carbon), petrographic composition, and oxidation levels can affect how coal is heated at low temperatures.4,5

Spontaneous combustion of coal can be described macroscopically. First, particles inside a coal pile are easily heated by the combination with oxygen. Thereafter, air flows to the interior of the coal pile because of the temperature difference between the inside and outside of the coal pile. Further, heat conduction, convective heat transfer, and heat transfer occur due to radiant heat transfer. If the heat accumulated inside the coal pile is higher than heat released from the surface of the coal pile, the temperature of the coal pile increases, triggering spontaneous combustion.6 The stages of spontaneous combustion are illustrated by Nijhof.7 In low-temperature environments, coal combines with oxygen, while slow oxidation occurs at 50 °C. In the second stage, from 50 to 250 °C, steady-state oxidation occurs, and depending on the rate of temperature increase and interaction with oxygen, thermal decomposition of coal occurs. In the third stage, self-sustained combustion begins.

In a previous study, petrographic analysis of spontaneous combustion of coal was carried out with maceral characterization. After low-temperature oxidation, vitrinite as the major maceral component could be changed in terms of reflectance and/or any other morphology that could be examined. Higher-ranked coals can be indicated by the vitrinite reflectance measurement due to the manifestation of temperature and pressure changes in the natural coal forming process.
the earth’s surface. The low-temperature oxidation experiment can be associated with natural environmental conditions that coal in the pile is subjected to. It can therefore be used in a laboratory-scale method to assess the changes of coal particles through their petrographic characteristics.

Due to the small reaction changes of coal under 100 °C, previous studies on spontaneous combustion have focused on the temperature and emission of a temperature of over 100 °C. A laboratory-scale experiment was conducted in a previous study as the main topic/theme. Further research on the reactivity of low-temperature oxidation and empirical research is needed. A bulk-scale experiment should be carried out as an empirical study. Therefore, this study was carried out at room temperature (25–75 °C) using kilogram units to describe real stockpiles in power plants. Thereafter, to determine the possibility of spontaneous combustion, a reaction rate of coal combustion was derived in an experiment designed by the Pusan National University in addition to an analysis of the reaction in the coal particles using petrographic characterization. Finally, each part of the analysis was compared and the possibilities of spontaneous combustion were derived.

In other words, the vitrinite reflectance and the morphology changes of coal were used as indicators to explain the altered conditions undergone by coal particles during the experiment. This could be used as an indicator of the tendency of certain coal ranks to have spontaneous combustion phenomena in this article.

2. EXPERIMENTAL SECTION

2.1. Coal Sample Preparation and Coal Characterization. The coals used in this study were dried and pulverized using a vibratory disc mill (RS 200, Retsch GmbH, Haan, Germany), after which they were separated using a sieve shaker (AS 200, Retsch GmbH, Haan, Germany) for particle sizes of 75–90 μm. Approximately 5 g of the sample was analyzed in the proximate analysis with a thermogravimetric analyzer (TGA 701) (LECO Co., St. Joseph, MI) based on the American Society for Testing and Materials (ASTM) D3172. The concluding analysis was carried out using a commercially available device (Leco-TruSpec Micro CHN5, LECO Co., St. Joseph, MI). Table 1 shows the coal properties considered in the low-temperature oxidation experiment and the corresponding petrographic analyses. These four coals have different fuel ratios (FRs); these ratios indicate the ease with which solid fuel can be ignited and subsequently gasified or oxidized depending on how the fuel is converted.

2.2. Low-Temperature Oxidation Experiment. Previous studies identified some causes of coal heating, one of the main reasons being oxidation of coals (1), followed by latent heat from phase change of moisture (2) and heat of sulfate ion formation (3). To calculate the oxidation rate of coal, Pusan Clean Coal Center (PCCC) has created a device to measure low-temperature oxidation. Figure 1 shows a schematic of low-temperature oxidation. This device called LOREM was created based on designs by Nordon from CSIRO.

\[
\text{coal} + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + 2500 \text{ (cal/g-coal)} \quad (1)
\]

\[
\text{coal/air} \rightarrow \text{coal/H}_2\text{O} + 5 \text{ (cal/g-coal)} \quad (2)
\]

\[
\text{FeS}_2 \text{(coal)} + \text{H}_2\text{O} + \text{O}_2 
\rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + 1 \text{ (cal/g-coal)} \quad (3)
\]

Analyzing the spontaneous combustion process is critical; for this, the oxygen consumption and temperature of the coal should be measured. LOREM manufactured by the Pusan University can be measured within a temperature range of −20 to 1250 °C in insulated and isothermal conditions. The temperature is measured using a K-type thermocouple at the center of the reactor. In addition, the mass of the reaction tube was tested with up to 5 kg of coal, and the gas supply was controlled using MFC. The oxygen concentration at the rear-end was measured over a wide range (0–60%) using a high-sensitivity (50 ppm) oxygen sensor. A perforated plate was placed at the bottom of the reactor to distribute air uniformly within. To calculate the oxygen consumption, 100 mL/min of air entered the reactor to enable the coal to oxidize sufficiently in the 40 L reactor and increase the oxygen residence time within the reactor. The particle size employed in this experiment was less than 2 mm, assuming that the oxidation of coal occurred in that particle size range.

The results obtained by LOREM pertain to the oxygen concentration consumed under certain temperature conditions. Therefore, when the experimental process is stable, the amount of oxygen consumption per liter from coal is calculated for each temperature condition. Using the linear regression form of the Arrhenius equation, the kinetic parameters can be obtained. Nordon et al. demonstrated through experimental verification that the oxidation reaction of coal and oxygen at low temperatures, which is the main reaction of spontaneous combustion, is governed by the Arrhenius equation, indicating

![Figure 1. Schematic of low-temperature oxidation experiment (LOREM).](image-url)

| Table 1. Coal Properties of the Low-Temperature Oxidation Experiment and Petrographic Analysis |
|-------------------------------|----------------|----------------|----------------|----------------|
| coal samples                  | A              | B              | C              | D              |
| Proximate Analysis (ad)       |                |                |                |                |
| inherent moisture (%)         | 8.86           | 6.14           | 2.45           | 1.53           |
| ash (%)                       | 3.84           | 4.11           | 13.14          | 13.17          |
| volatile matter (%)           | 47.53          | 44.10          | 35.23          | 25.23          |
| fixed carbon (%)              | 39.77          | 45.65          | 49.18          | 60.07          |
| Ultimate Analysis (daf)       |                |                |                |                |
| C (%)                         | 62.40          | 68.40          | 77.90          | 83.87          |
| H (%)                         | 5.31           | 5.30           | 5.40           | 4.73           |
| O (%)                         | 27.50          | 24.00          | 14.30          | 8.91           |
| N (%)                         | 0.85           | 1.30           | 2.00           | 1.79           |
| S (%)                         | 1.94           | 1.00           | 0.40           | 0.70           |
| FR (fuel ratio, FC/VM)        | 0.84           | 1.03           | 1.40           | 2.38           |
that the reaction rate of oxygen tends to increase as the temperature increases at a low temperature. In addition, the Elovich equation could be used for the absorption of oxygen, which could have a decelerating effect at a low temperature. After these two effects, the oxidation reaction rate for coal and oxygen was derived as shown in equations below.\textsuperscript{10}

\[
\frac{dq}{dt} = r_0 A \exp\left(\frac{-(E + Bq)}{RT}\right) \text{(h}^{-1}) \tag{4}
\]

\[
A \exp\left(-\frac{E}{RT}\right) = 1 \text{ (when } T = T_0) \tag{5}
\]

\[
\frac{dT}{dt} = \frac{H}{C_p} \frac{dq}{dt} (K h^{-1}) \tag{6}
\]

\[
q = \frac{C_p \left(\frac{T + T_0}{2}\right)}{H} (T - T_0) \tag{7}
\]

\[
\frac{E/RT_0 - E/RT}{B/C_p (\frac{T + T_0}{2})} = \frac{(T - T_0)}{H} \tag{8}
\]

In these equations, \(q\) is the amount of oxygen taken up per unit weight of coal at time \(t\) (h), \(r_0\) refers to the rate of oxidation at 20 °C, and \(A\) is the pre-exponential factor, here taken as \(A = e^{E/RT}\) so that eq 5 can be derived. \(E\) is the activation energy, which can be measured in LOREM; \(R\) is the universal gas constant; \(T\) is actual temperature; and \(T_0\) is the initial temperature. \(B = bRT\), where \(B\) is the Elovich constant,\textsuperscript{12} which is independent of temperature, but \(b\) may depend on temperature. \(H\) is referred to as heat of reaction and \(C_p(T)\) is the specific heat capacity as a function of temperature. The specific heat capacity is linearly related to temperature, and under adiabatic conditions, eq 6 can be integrated to eq 7. These equations can indicate the two processes of accelerating effect of temperature and decelerating effect of the extent of oxidation (Elovich equation). Furthermore, the transition between these two processes occurs when the \(B\) is so large that eq 8 could be derived when eqs 4, 6, and 7 were combined and calculated mathematically in reference to Nordon.\textsuperscript{10} In this study, the amount and rate of oxidation is the main focus, which included both the accelerating effect and decelerating effect that could occur simultaneously. Therefore, the diffusion of coal oxidation was not greater than that at high temperatures; hence, a kinetic-controlled regime could be assumed, and the linear return was appropriate at low temperatures.\textsuperscript{12}

2.3. Petrographic Analysis after Low-Temperature Oxidation. The petrographic analysis conducted in this study covered two steps. The first step was the sample preparation process and the second was the petrography sample analysis via measurement of vitrinite reflectance measurement and coal maceral morphology change with the point-counting method. Coal samples derived from the low-temperature oxidation experiment were prepared for petrography analysis via the cold mounting method in a standard cylindrical molder using liquid co-cast resin. After being perfectly hardened overnight at 25 °C, the blocked samples were ready for grinding and polishing to generate scratch-free and polished sample blocks.\textsuperscript{15}

In terms of petrography characterization in this study, two major elements were to be derived: the vitrinite reflectance change and the maceral morphology change, as mentioned in the Introduction section. Both measurements were obtained using an Axioscope-A0 microscope (Carl-Zeiss) equipped with white and UV light sources, a reflectophotometer from CRAIC system, and software specifically for the measurement of coal-vitrinite reflectance. The microscope was equipped with three different objective lenses (10X, 20X, and 50X magnification) with two 10X eyepiece lenses. During this study, the examinations of both the vitrinite reflectance and maceral changes were performed using a total magnification of 500X (50X objective lens × 10X eyepiece lens). Maceral morphology changes were identified based on examinations from 500 points representative of a polished coal sample surface using a semiautomatic stepping stage point counter attached to the microscope unit.

3. RESULTS AND DISCUSSION

3.1. Kinetics and Reaction Rates of Coal during Low-Temperature Oxidation. Figure 2 shows the \(O_2\) concentration percentage (after the air emission from the reactor) with a red line and the temperature of the reactor with a black line. This data is an example of the raw data of case 1 (50 °C experiment). In the graph, three periods of this experiment are indicated, namely, the reactor preheating period, reactor scavenging period, and steady-state (stable) period. In the reactor preheating period, the coal is heated up by the reactor’s heater, and this process requires more than 30 h. Only nitrogen was allowed into the reactor at that time, hence the oxidation of coal did not occur during this period. Following the reactor preheating period, the reactor scavenging period occurs. In this period, air insertion by MFC and coal oxidation commenced. However, the result from this period is treated as trivial data because the air and nitrogen (inserted in the previous period) are mixed haphazardly; thus, it cannot be determined as to which period the nitrogen was inserted in. Finally, in the steady-state period, the oxygen percentage becomes stable and temperature of the experiment is set (25, 50, and 75 °C). Herein, data can be obtained for the stable condition for several hours, and the average oxygen content for this stable period can be calculated. Moreover, the difference in oxygen concentration between the reactor preheating period and stable period could indicate the quantity of oxygen consumed.

Table 2 shows the elements used to derive the kinetics in the low-temperature area of each individual coal. The values of the setting and actual temperatures presented in Table 2 differ
of the coal samples, and Table 3 shows both the activation energy (oxidation were derived using these factors based oneqs 4

The kinetics of coal at low-temperature period. The value of O₂ concentration can be obtained as a

obtained for approximately 10 h after entering the steady result

therein. The average value of temperature and oxygen is

measured oxygen consumption and the temperature value

1/

1/

1/

\text{RT}

\text{ln(d}x/\text{dt}) \ (\text{kgO}_2/\text{kg-coal-s}) \ -20.11 \ -17.73 \ -16.52

| actual temperature (°C) | oxygen consumption (kgO₂/kg-coal-s) | 1/\text{RT} (mol/kJ) | \text{ln(d}x/\text{dt}) \ (\text{kgO}_2/\text{kg-coal-s}) |
|------------------------|------------------------------------|----------------------|-----------------------------------------------|
| actual temperature (°C) | oxygen consumption (kgO₂/kg-coal-s) | 1/\text{RT} (mol/kJ) | \text{ln(d}x/\text{dt}) \ (\text{kgO}_2/\text{kg-coal-s}) |
| actual temperature (°C) | oxygen consumption (kgO₂/kg-coal-s) | 1/\text{RT} (mol/kJ) | \text{ln(d}x/\text{dt}) \ (\text{kgO}_2/\text{kg-coal-s}) |

slightly because of which the coals have different definitions. The setting temperature refers to the temperature setting of the heaters, and actual temperature refers to the temperature of the coal at which low-temperature oxidation and heat release occur. This is similar to eq 1, which indicates the main cause of low-temperature combustion. To derive the kinetics, the values 1/\text{RT} and \text{ln(d}x/\text{dt}) should be obtained, which indicate the measured oxygen consumption and the temperature value therein. The average value of temperature and oxygen is obtained for approximately 10 h after entering the steady result period. The value of O₂ concentration can be obtained as a percentage, where the amount of oxygen can be calculated by converting it into a value using the ideal gas equation (PV = mRT). This is done by deriving the value of \text{ln(d}x/\text{dt}) of kinetic to mass flow per coal (kgO₂/kg-coal-s), which indicates oxygen consumption. The kinetics of coal at low-temperature oxidation were derived using these factors based on eqs 4−5.

Figure 3 shows the low-temperature kinetics (25−100 °C) of the coal samples, and Table 3 shows both the activation energy (E_a) and frequency factor (A). The FR has been used to compare the coal samples, and all factors affected in low-temperature oxidation have been compared. In general, the smaller the value of the activation energy, the greater the reactivity. However, the results below show that the activation energy is the highest in the case of coal A with the lowest FR value. In contrast, the frequency factor value of coal A was the highest. The above results imply that the activation energy and frequency values of kinetics are difficult to determine for low-temperature oxidation. Therefore, we employed \( k \) (reaction constant), an indicator of oxygen reactivity, as a reference to the Arrhenius eq 9 for reverse estimation.

\[
k = A \exp(-E_a/RT)
\]  

(9)

The graph shown in Figure 4 presents a correlation between the FR and \( k \) (constant of reaction) values according to temperature. Each point with the same FR indicates the same kind of coal. At 25 °C, when the FR of each coal sample increases, the reaction constant also increases. At 50 °C, regardless of the FR, the \( k \) value was constant. At 75 °C, the smaller the FR value, the higher the likelihood of \( k \) being extremely high. From these results, the value of activation energy at 25 °C tends to be the opposite of the expected value; based on this, we can estimate that oxygen molecules could be absorbed into the coal without an actual oxidation reaction. A study by Wang et al. shows that at low temperature, oxidation and physical and chemical absorption occurred following a small thermal reaction. Therefore, to eliminate the initial effect and mainly focus on analyzing the change of the reaction between the constant reaction of 25 °C (as the initial setting temperature) and those of 50 and 75 °C, the normalized \( k \) value was derived as the difference between the reaction constant of the initial setting temperature of 25 °C and those at 50 and 75 °C. In terms of the normalized \( k \) value, the reactivity of the coal was high for lower values of FR.

### 3.2. Petrography of Origin Coal

The objective of this study was to examine three coal samples of different ranks; two samples exhibiting similar values of vitrinite reflectance were known to be susceptible to spontaneous combustion because of characteristics, such as high moisture content, friability in open-air environments, high oxygen content, and volatility, that can increase the likelihood of the oxidizing effect. The vitrinite reflectance measurements (\( R_m \)) of the three coal

![Figure 3. Low-temperature oxidation kinetics of each coal sample.](https://dx.doi.org/10.1021/acsomega.0c00840)
D; huminite (<0.5% reticulated with LOREM under three dimensions of the coal samples were recorded after they were treated with LOREM under three different temperatures, namely, 25, 50, and 75 °C. The initial setting temperature was 25 °C as this was the original coal condition. Several studies have examined low-temperature oxidation of coal and vitrinite reflectance since vitrinite is the major maceral component in coal samples. Table 5 shows the vitrinite reflectance value for each coal sample, including the original values and the changed values after oxidation, with the total percentage of the changes relative to the original reflectance. As expected from the coal rank measurement based on the original mean random vitrinite reflectance (R₀), coal A had the lowest coal rank (R₀: 0.35%). It had the strongest impact on the vitrinite reflectance changes for both 50 and 75 °C setting temperature conditions. This might occur because of the improvement of the basic chemical characters of the coal, such as higher moisture content, because of which the hydrogen molecules in the moisture content react with the oxidizing agent during the experiment. Otherwise, in a coal pile environment, the heat released upon oxidation evaporates the moisture, and the liquid-to-gas reaction releases energy, increasing the particle temperature and finally commencing the self-heating phenomena. The vitrinite reflectance change of coal C was lower than that of coal A; this is an interesting trend because coal C did not follow the general "rules" regarding coal rank for spontaneous combustion tendency. From Table 3, the order of the coal rank after coal A should ideally be coal B, but based on the vitrinite reflectance changes, coal C shows stronger vitrinite reflectance changes than that of coal B. Moreover, coal C has a lower moisture content than that of coal B; therefore, we should refer to another coal characteristic that can influence the propensity of self-heating or spontaneous combustion in such cases.

Coal is composed of heterogeneous organic–inorganic materials, which strengthens the results of various characteristics included in vitrinite reflectance changes during coal processing technology. Therefore, we should consider the existence of the organic and inorganic materials that constitute coal. Petrography analysis made it possible to distinguish the existence of the organic and inorganic materials that constitute the coal. Petrography analysis made it possible to distinguish the organic and inorganic materials that constitute the coal. Petrography analysis made it possible to distinguish the existence of the organic and inorganic materials that constitute the coal. Petrography analysis made it possible to distinguish the organic and inorganic materials that constitute the coal. Petrography analysis made it possible to distinguish the existence of the organic and inorganic materials that constitute the coal. Petrography analysis made it possible to distinguish the organic and inorganic materials that constitute the coal. Petrography analysis made it possible to distinguish the existence of the organic and inorganic materials that constitute the coal.

samples (Table 4) show the different ranks of coal with different maceral constituents. From the results of the petrographic analyses considering the basic analysis of the coals, shown in Table 1, coal A and coal B were classified as liptinite-A, coal C as sub-bituminous, and coal D as high-volatile bituminous-C, based on the coal classification by rank and indices of organic maturity, modified from ASTM (1981), Techmuller (in Stach et al., 1982), Dow (1977), and Cameron (1989).

### 3.3. Petrography Characterization of the Oxidized Sample

#### 3.3.1. Vitrinite Reflectance Change of Coal after Low-Temperature Oxidation

Vitrinite reflectance measurements of the coal samples were recorded after they were treated with LOREM under three different setting temperatures, namely, 25, 50, and 75 °C. The initial setting temperature was 25 °C as this was the original coal condition. Several studies have examined low-temperature oxidation of coal and vitrinite reflectance since vitrinite is the major maceral component in coal samples. Table 5 shows the

| Table 3. Activation Energy and Frequency Factors of Oxygen Consumption for Each Coal Sample |
|-----------------------------------------------|
| coal sample | A | B | C | D |
| activation energy (kJ/mol) | 66.17 | 29.57 | 28.89 | 8.74 |
| frequency factor (kgO₂/kgcoal-s) | 5.25 × 10⁵ | 6.70 × 10⁴ | 3.68 × 10⁴ | 2.87 × 10⁻⁷ |

| Table 4. Vitrinite Rank and Maceral Analysis of Coal Samples in MMF |
|-----------------------------------------------|
| coal-vitrinite rank (R₀ (%)) | huminite/vitrinite (%) | liptinite (%) | inertinite (%) |
| A—0.35 | 91.27 | 3.36 | 5.37 |
| B—0.40 | 64.67 | 2.67 | 32.67 |
| C—0.44 | 73.0 | 3.0 | 14.0 |
| D—0.60 | 83.0 | 1.0 | 16.0 |

"Mineral matter free (MMF). Huminite: coal A, B, C; Vitrinite: coal D; huminite (<0.5% reflectance), vitrinite (≥0.5% reflectance)."

#### 3.3.2. Correlation between FR and k (constant of reaction) according to temperature (a) and correlation between FR and normalized k considering absorption (b).

![Figure 4](http://dx.doi.org/10.1021/acsomega.0c00840)
Figure 5. Histogram of vitrinite reflectance distribution for each sample A (a), B (b), C (c), and D (d).

| Coal | Homogeneous reflectance changes | Oxidation rims | Unaltered material |
|------|--------------------------------|----------------|-------------------|
| A    | ![Image](imageA_homogeneous)   | ![Image](imageA_oxidation) | ![Image](imageA_unaltered) |
| B    | ![Image](imageB_homogeneous)   | ![Image](imageB_oxidation) | ![Image](imageB_unaltered) |
| C    | ![Image](imageC_homogeneous)   | ![Image](imageC_oxidation) | ![Image](imageC_unaltered) |
| D    | ![Image](imageD_homogeneous)   | ![Image](imageD_oxidation) | ![Image](imageD_unaltered) |

Figure 6. Pictures indicating morphology changes and unaltered materials in coal A, B, C, and D.
Table 6. Maceral Morphology Evaluation after LOREM

| Unit % Changes          | A     | B     | C     | D     |
|------------------------|-------|-------|-------|-------|
| Homogeneous reflectance changes | 50 °C | 75 °C | 50 °C | 75 °C | 50 °C | 75 °C | 50 °C | 75 °C |
|                         | 45.7  | 4     | 6.4   | 24    | 35.2  | 0     | 1.6   |       |
| Oxidation rims          | 5.8   | 1.3   | 12.6  | 10.7  | 6.3   | 4.0   | 0     |       |
| Unaltered material      | 48.5  | 32.9  | 75.2  | 81    | 65.3  | 58.5  | 96    | 98.4  |

visible in the histogram in Figure 5, which represents the vitrinite distribution for each LOREM setting condition, and the gap between each belonging to LOREM conditions that becomes the basis for identifying which coal sample represents the highest vitrinite reflectance changes. In this case, coal A shows a significant graph shift between the original vitrinite reflectance and the reflectance after oxidation.

3.3.2. Maceral Morphology Change Evaluation. Besides the vitrinite reflectance changes, some vitrinite also undergo morphology alteration due to the effect of temperature and oxygen on the reacting gas from the LOREM measurement with respect to coal particles. As pointed out in previous research, maceral morphology can also be used to indicate the tendency of coal spontaneous combustion.7,17,18 Figure 6 indicates each morphology change such as homogeneous reflectance changes, oxidation rims, and unaltered material of each coal. As shown in Figure 6, homogeneous reflectance changes can be confirmed where UV reflections take place as whole parts in some areas, as shown in Figure 6. Oxidation rims could also be detected, which are shown as lines in the figure. Table 6 shows the results of altered maceral from coals A, B, C, and D after manual petrographic examinations from 500 representative points, respectively. As expected, also confirming the previous result, coal A has the strongest effect on LOREM by showing the largest percentage of altered maceral for both setting temperatures. The order of the maceral morphology alteration magnitude between samples was coal A > C > B > D, confirmed by the previous vitrinite reflectance changes. For the petrography characterization of coal spontaneous combustion tendencies, evaluations should be performed to integrate both vitrinite reflectance change measurement and maceral morphological analysis. If only one of the analyses is performed, random behavior results could be obtained due to the dependency correlation between coal character parameters such as coal basic analysis (proximate—ultimate) and the coal petrography characteristics. The result of maceral alteration was obtained from previous research and was grouped into primary and secondary alterations.7 From LOREM proposed in this study, the result of maceral alteration evaluation for each sample shows that only primary alteration can be found in all samples, and this result might occur due to lower temperature settings than those employed in previous research. In this study, the focus of the research was to study the effect of oxidation at 100 °C.

4. CONCLUSIONS AND SUMMARY

Low-temperature oxidation experiments and petrographic analyses were conducted in a low-temperature range. To modify the kinetics of low-temperature oxidation, oxidation rate and temperature were measured using LOREM, fabricated by the Pusan National University. Following this, the activation energy and frequency factor were derived for low temperature, and the constant of reaction and reactivities of coal were obtained using the Arrhenius equation. To analyze the maceral characteristics, a petrograph test device, an Axioscope-A0 microscope (Carl–Zeiss) equipped with white and UV light sources, and a reflectophotometer from CRAIC system were also used. The following are the main results obtained and the subsequent conclusions drawn thereafter.

1. Regarding correlations between the rate constant of reaction and FR for coal samples A−D, the FR rate increases and the rate constant of reaction (k) increases at setting temperature, 25 °C. However, k is stable at 50 °C and decreases at 75 °C, implies that when the coal was of high rank, it did not react with oxygen easily. The reason for the 25 °C value tending to be the opposite of the expected value is that oxygen molecules can be absorbed inside the coal. On eliminating the effect and mainly focusing on analyzing the change of the reaction between the constant reaction of 25 °C as the initial setting temperature and those of 50 and 75 °C, the normalized k value was derived by subtracting the reaction constant of the initial 25 °C temperature. The normalized k also indicated that the higher the value of FR, the lower the reactivity.

2. In maceral analysis, vitrinite reflectance and morphology analyses were conducted. Moreover, coal was extracted from the sample used in the low-temperature oxidation experiment. The objective of the research was to obtain four coal samples, which have different ranks. Herein, sample A had the lowest rank and sample D had the highest rank, which is in correlation to the FR sequence. The lowest coal rank (Rc: 0.35%) belongs to coal A and has the strongest impact on the vitrinite reflectance measurement both for 50 and 75 °C setting temperature conditions. Coal samples B and C could also be obtained having the same tendency as expected. However, the next tendency of vitrinite reflectance changes belonged to coal C after A, which was quite interesting, because coal C did not follow the general coal rank to spontaneous combustion tendency rules. Regarding the moisture content, coal C had a lower moisture content than coal B; therefore, in this regard, we should refer to another coal characteristic that could better influence the propensity of self-heating or spontaneous combustion.

3. The order of the maceral morphology alteration magnitude between samples was A > C > B > D, as confirmed by previous vitrinite reflectance changes. From the LOREM measurement proposed in this study, the result of maceral alteration evaluation for each sample shows that only primary alteration can be found in all samples.

4. When comparing the two above results of low-temperature oxidation and its petrographic analysis, it was found that the normalized k value and VR changes could be inferred to similar trends. Therefore, it can be concluded that understanding the correlation between the reactivity of coal and the petrographic analysis can
help to predict the possibilities of spontaneous combustion of each coal sample.

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This manuscript was written through contributions of D.-G.L. as a first author. D.-G.L., Y.I., and K.-H.P. designed and conducted the experiment. D.-G.L., D.-G.L., and S.-M.K. analyzed the data. D.-G.L. performed validation writing.

Notes
The authors declare no competing financial interest.

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■ ABBREVIATIONS USED

TGA, thermogravimetric analysis; LOREM, low-temperature reaction rate measurement; VM, volatile matter; VR, vitrinite reflectance; \( R_{\text{w}} \), mean random vitrinite reflectance; \( k \), constant of reaction; MFC, mass flow controller; \( E_a \), activation energy; A, frequency factor; FR, fuel ratio

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