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Comparison of spontaneous combustion susceptibility of coal dried by different processes from low-rank coal

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Abstract−We compared the susceptibility to spontaneous combustion of low-rank coals dried by four different processes: flash drying, fluidized bed drying, non-fried carbon briquetting, and coal-oil slurry dewatering. The coals were characterized by FT-IR and XPS analysis. A crossing-point temperature (CPT) was estimated as a comparison criterion of the susceptibility of the coals to spontaneous combustion. O_2, CO, and CO_2 emissions during the CPT measurement were also compared. The FT-IR and XPS analysis revealed that some of the oxygen functional groups on the surface of the coal were removed when the coal underwent the drying process. This phenomenon was particularly noticeable in the coal dried by oil. Accordingly, the CPT of the coal that went through this drying process was high. Among the samples, the coals dried by oil showed the highest CPT.

Keywords: Low-rank Coal, Crossing-point Temperature, Drying, Spontaneous Combustion, Oxidation

INTRODUCTION

There has been a growing need for the utilization of low-rank coal because of the short supply and increasing prices of high-rank coal. Because low-rank coal has a high moisture content and a low heating value, if it is utilized in a system that has been designed for high-rank coal without any adaptation, it decreases the efficiency and increases the load on the facility. Also, low-rank coal is basically characterized by a high amount of oxygen functional groups on the surface of the coal. These functional groups triggered spontaneous combustion by promoting the accumulation of the heat caused by moisture adsorption and oxidation. Therefore, special care is required for the handling of low-rank coal. These characteristics of low-rank coal will determine the environmental and economic costs.

To address these problems, the technology of low-rank coal has recently been upgraded. In particular, owing to its technical availability, an upgrade using a drying process was developed.

The widely-known drying technologies used in coal are Binderless Coal Briquette (BCB) in Australia [1,2], which is a flash drying process; DryFining™ in the USA [3,4]; WTA in Germany, which stands for *Wirbelschicht-Trocknung mit interner Abwärmenutzung* (fluidized bed drying with internal heat recovery) [5,6]; and upgraded brown coal (UBC) in Japan [7-9], which is a coal-oil slurry dewatering process. Drying processes using gases, such as air, flue gas, or steam have the advantage of being simple, while the drying process using oil has a short drying time and a high removal rate of moisture due to the excellent heat transfer of oil medium.

In a previous study, we reported that the drying process applying coal-oil slurry dewatering method not only increases the heating value of low-rank coal, but it also suppresses the susceptibility of the coal to spontaneous combustion and the re-adsorption of moisture to some degree [10]. Even though the degree of suppression of the susceptibility to spontaneous combustion is expected to vary according to the drying method, comparing the effect of the various drying processes on the susceptibility of the coal to spontaneous combustion has not been studied. It is necessary to evaluate the degree of the suppression of the susceptibility of the coal to spontaneous combustion based on the drying method, due not only to the cost of the drying process itself, but also because the suppression of the susceptibility of the coal to spontaneous combustion by the drying process is an important criterion in choosing which drying process to use.

To estimate the oxidation characteristics of coal, methods of evaluating temperature or mass variation of coal by oxidation [11-15], and methods analyzing the amount of O_2 consumed or the amount of CO/CO_2 generated by the oxidation of coal [16-20] are usually applied. Among the above methods, because of the simplicity, measuring and comparing a crossing-point temperature (CPT) to indicate the onset temperature of self-heating by oxidation and heat accumulation has been widely used to characterize the susceptibility of coal to spontaneous combustion [21-24].

We compared the susceptibility of low-rank coal to spontaneous combustion according to treatment by different drying processes. Four drying processes were applied for comparison: flash drying (FD) using gas, fluidized bed drying (FBD), non-fried carbon briquetting (NFCB) using oil, and coal-oil slurry dewatering (COSD). The first two processes use gas as a drying medium, whereas the other two use oil. Raw coal and dried coal samples were characterized by proximate analysis, FT-IR analysis, and XPS analysis. The CPT was estimated as a comparison criterion for the susceptibility of the coal samples to spontaneous combustion. O_2 consumption and CO and CO_2 emission during the CPT measurement were also

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compared.

MATERIALS AND METHODS

1. Materials

Indonesian lignite, Eco coal, was used in this study. The raw coal was prepared by crushing the lump coal into pieces 180-425 μm. The raw coals were then dried using four different processes of FD, FBD, NFCB, and COSD, and named FD coal, FBD coal, NFCB coal, and COSD coal, respectively.

The FD coal was dried instantly by injecting coal particles into a riser pipe 40 mm in diameter and 5,000 mm in height in which hot flue gas at a temperature of 400 °C flowed at 20 m/sec. The coal particles dried in the riser were collected in a cyclone. Although the drying temperature was high, because the contact time was very short, there was very little loss of coal caused by the volatilization of the coal. [25].

The FBD coal was dried by fluidizing coal particles with nitrogen in a multi-chamber fluidized bed dryer. The fluidized bed dryer consisted of three fluidized beds 500 mm in height arranged in series. The coal feeding rate at the inlet was 16 kg/hr. The inlet velocity of fluidizing nitrogen was 0.6 m/sec. The inlet and the outlet temperature of the nitrogen were 150 °C and 40 °C, respectively. This process requires a long drying time, but drying can be done even at a low temperature [26].

To make NFCB coal, the raw coal particles were mixed with kerosene to which waste polyethylene was added (0.5 wt%) at 100 °C in a proportion of 1 : 1, and then the coal particles were filtered. The remaining wet solid was dried in a disc-type drier at 160 °C to obtain the dried NFCB coal. In the process, the kerosene disperses the waste polyethylene, rather than taking the role of a heat transfer medium [27].

To produce COSD coal, we mixed coal particles with kerosene to which asphalt was added (0.5 wt%) in a proportion of 1 : 1 to make slurry and retained at 140 °C under 0.3 MPa for 30 minutes. To obtain the dried coal, the liquid was then vaporized from the slurry at 160 °C under nitrogen atmosphere. In the process, kerosene acts as both heat transfer medium and dispersing asphalt [10].

The waste polyethylene and the asphalt are added for a stabilization effect, which prevents re-adsorption of moisture or oxidation after drying the kerosene.

The dried coals were sieved again to achieve the same size distribution as that of the raw coal for use in the experiment.

2. Apparatus for CPT and Gas Measurement

When a coal sample is placed in an oven of a predetermined temperature and then is exposed to air, while the oven temperature increases at a constant rate, the temperature of the coal will exceed that of the oven at a certain point due to the coal's self-heating. This point is defined as CPT.

Fig. 1 shows a conceptual diagram of the apparatus for CPT and gas measurement. Two vessels containing coal samples are located inside an oven. Nitrogen or air is selectively supplied to each vessel by manipulating the valve. The gas is supplied to the vessel by controlling the flow with a mass flow controller (MFC). When it passes through the copper tube coil inside the oven, the temperature of the gas is adjusted to match the oven temperature. The temperature of the oven and the coal inside each vessel is measured by T-type thermocouples. The gases that pass through the vessels are sent to either the GC (6890N, Agilent Technologies) to measure the components, or to the mass flow meter (MFM) to measure the flow rate after reaction, according to the selected 4-way crossover valve location, which changes periodically. The moisture trap and particulate filter are attached to the front area of the GC and the MFM.

The O_2, CO, and CO_2 emitted from each vessel was measured in the GC to which the thermal conductivity detector and two columns (60/80 Molecular Sieve 13X, 80/100 Porapak N, SUPELCO)

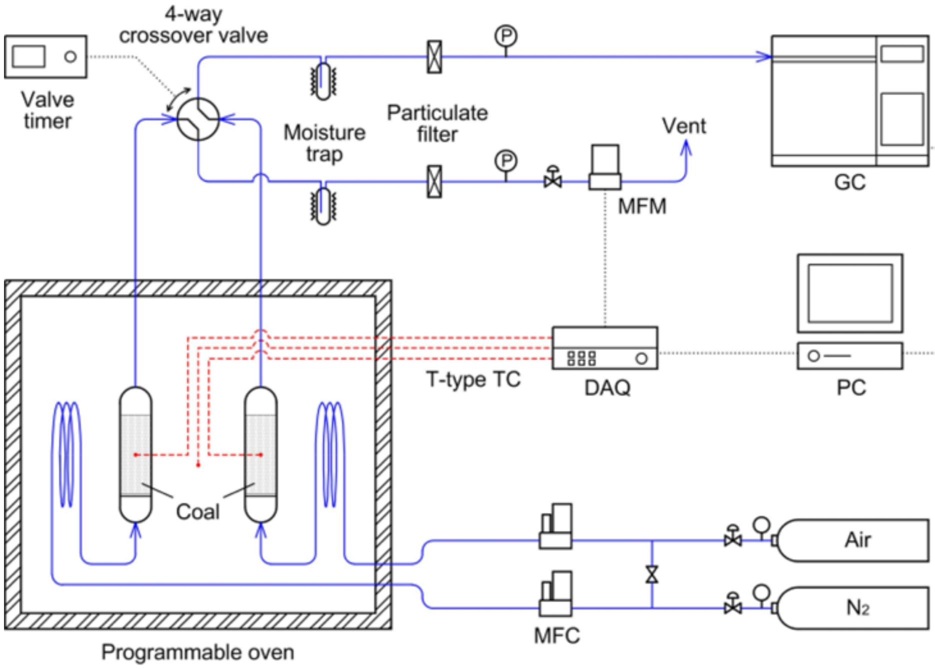

Fig. 1. Experimental setup for CPT and gas measurement.

were installed.

3. Experimental Procedure for CPT and Gas Analysis

Not only the dried coal samples, but also the raw coal sample was dried at 107 °C for five hours under a nitrogen atmosphere before the experiment to remove any effect that might be caused by moisture.

Two vessels, each containing 35 g of the same coal sample, were installed in an oven and kept for two hours under nitrogen to achieve the temperature equilibrium at 40 °C. The oven was then heated at 0.5 °C/min ramp rate while supplying 75 cm^3/min air to the one and the same amount of nitrogen to the other vessel as a reference.

During the heating, the vessel temperature typically lags behind the oven temperature, due to relatively high heat capacity of the coal. However, a steep increase of the vessel temperature is observed when the coal in contact with air is self-oxidized. The vessel temperature then exceeds the oven temperature at some point, which is defined as CPT.

In the GC, helium was used for both the carrier gas and the reference gas. The measurement was done every 15 minutes at isothermal conditions of 35 °C.

RESULTS AND DISCUSSION

1. Basic Properties of Coals

Table 1 shows the basic properties of the coal samples used in the experiments. The raw coal has high oxygen and high volatile matter content, which are typical characteristics of low-rank coal. The data did not show notable differences between the samples, which indicates that no radical changes in basic properties occurred in the drying processes.

2. FT-IR Analysis

Fig. 2 represents the FT-IR spectra of the coal samples and the additives that were used in the drying processes. The spectra of the FD coal and the FBD coal dried by gas flow were similar to that of the raw coal. With regard to the FD coal, a study reported tar formation on the surface due to the coal's instant disclosure to high temperature gas during the drying process [28], but there was no finding that supports that result in this FT-IR analysis.

The NFCB coal and the COSD coal that were dried by oil showed higher C-H stretching peaks at 2,920 and 2,850 cm^{-1} and lower C-O stretching peaks at 1,100 and 1,033 cm^{-1} than did the raw coal (Fig. 2(b)). As for the reason for the high C-H peaks of the NFCB coal, and the COSD coal, it was assumed that the high molecular additives, such as polyethylene and asphalt which have high C-H stretching peaks, remained on the surface of the coal. As for the low C-O peaks, we assumed that the functional groups having this structure were removed by the oil, or coated by the additives, during the drying process.

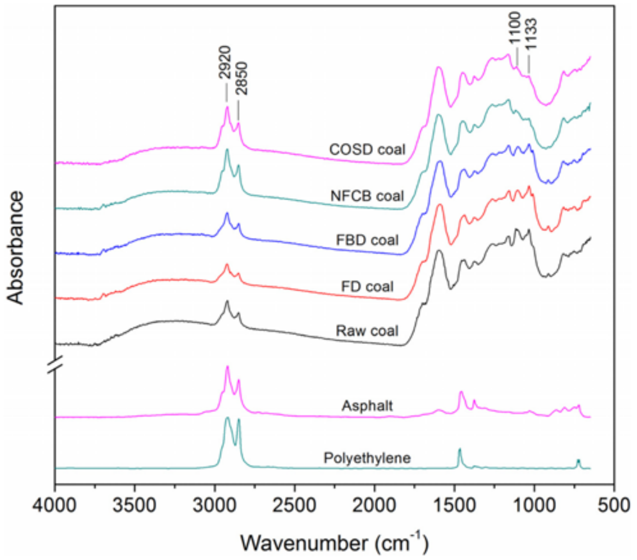

Fig. 2. FT-IR spectra of coal samples and additives.

3. XPS Analysis

Fig. 3 shows the XPS spectra of the raw coal and the dried coal. The XPS spectra were curve-fitted by using XPSPEAK v4.1 software with a Gaussian/Lorentzian product function (50% Lorentzian maximum). The original spectrum was resolved into five peaks at 284.6, 285.3, 286.3, 287.5, and 289.0 eV, which were assigned to C-C, C-H, C-O, C=O, and O-C=O forms, respectively [29]. The resolved XPS spectra of the raw coal showed that the raw coal had a large amount of carbon-oxygen content on the surface. An extended tail in a high binding energy region, which is responsible for a broad O-C=O peak, indicated that there are not only five forms of carbon considered, but also other different carbon-oxygen forms on the surface of the coal.

Although it was not shown notably in the FT-IR analysis, the XPS analysis showed that the C-O, C=O, and O-C=O content of the FD coal (Fig. 3(b)) and the FBD coal (Fig. 3(c)) decreased to some degree compared to the raw coal. The C-O, C=O and O-C=O contents of the NFCB coal (Fig. 3(d)) and the COSD coal (Fig. 3(e)) were much less than those of the raw coal and even less than those of the FD coal and FBD coal.

Assuming that the C-C peak area of all samples was constant,

Table 1. Basic properties of coal samples

Coal sample	Ultimate analysis (wt%, daf base)					Proximate analysis (wt%, dry base)			Heating value (MJ/kg, N_2 dry)
	C	H	N	S	O	VM	Ash	FC	
Raw coal	71.88	5.31	0.92	0.13	21.76	54.98	4.24	40.78	27.21
FD coal	72.74	5.14	0.87	0.16	21.09	53.59	5.30	41.11	27.01
FBD coal	73.08	5.18	0.87	0.18	20.69	55.37	4.82	39.81	26.85
NFCB coal	72.77	5.74	0.78	0.18	20.53	56.38	3.72	39.90	28.96
COSD coal	74.26	6.07	0.77	0.17	18.73	58.31	3.33	38.36	30.29

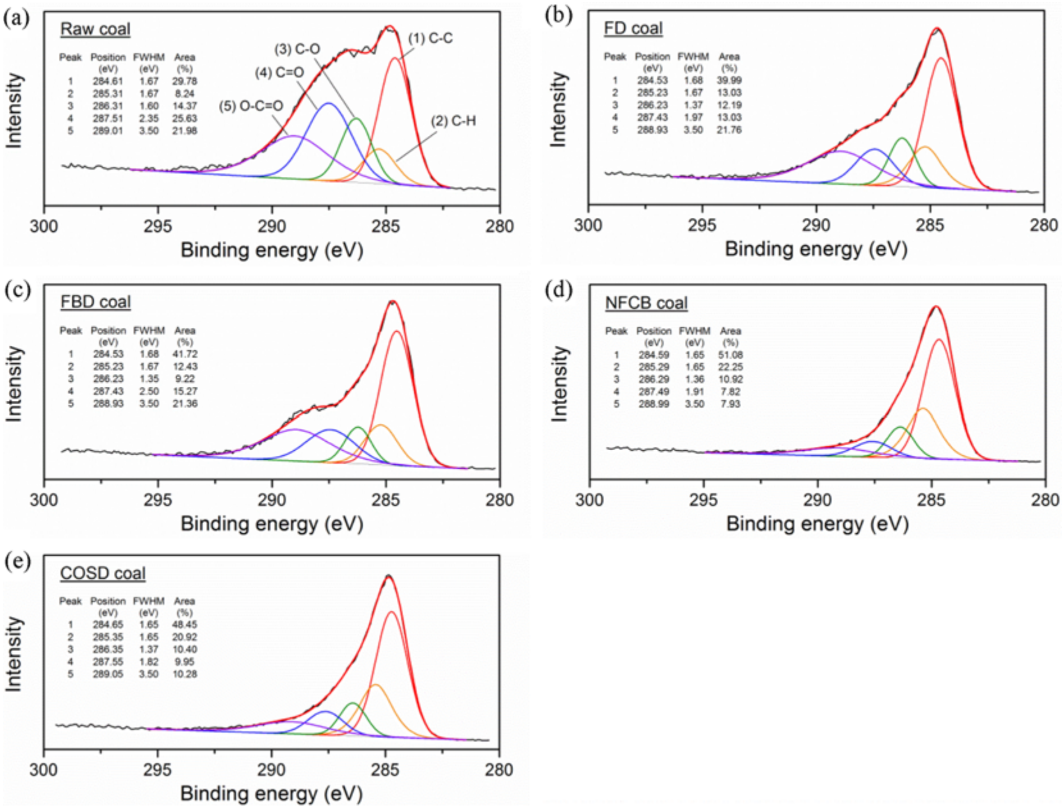

Fig. 3. XPS C1*s* spectra of (a) Raw coal, (b) FD coal, (c) FBD coal, (d) NFCB coal, and (e) COSD coal.

the sum of the values of the C-O, C=O, and the O-C=O peak area in the case of the FD coal, and the FBD coal, decreased by 50% compared to those of the raw coal, and by about 70% in the case of the NFCB coal and the COSD coal. In contrast, the C-H peak area of the NFCB coal, and the COSD coal, increased about by 55% compared to those of the raw coal. These trends coincided with the results of the FT-IR analysis.

4. CPT Measurement

Fig. 4 shows the results of the CPT measurements of the raw coal and the dried coals. In the figure, the small dots represent the results that were repeated 6-7 times on each coal sample. The hollow square indicates the mean value of the measurement by sample. The CPT of the raw coal was 132.5 °C on average, and that of all dried coal was higher than the raw coal. An increase in CPT means that the temperature at which self-heating starts to occur gets increased, and it also means that spontaneous combustion will occur less often.

Among the dried coals, the CPTs of the coal dried by oil were higher than those of the coal dried by gas. The CPT of the FD coal was similar to that of the FBD coal, and the CPT of the NFCB coal was similar to that of the COSD coal in the range of error. It is consistent with the trend in the XPS analysis where the values of C-O, C=O and O-C=O peaks decreased. That is, it can be interpreted that,

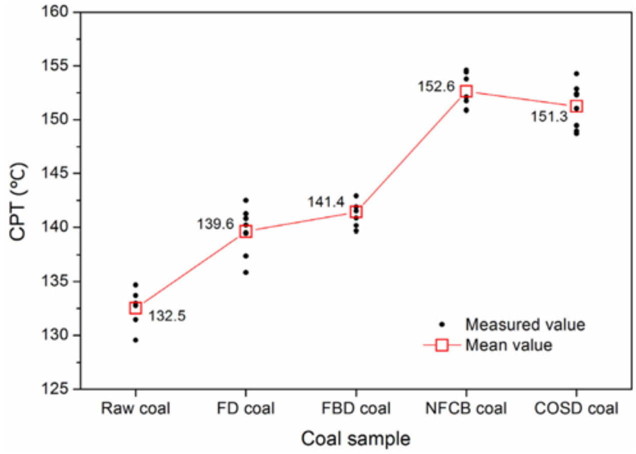

Fig. 4. CPTs of coal samples.

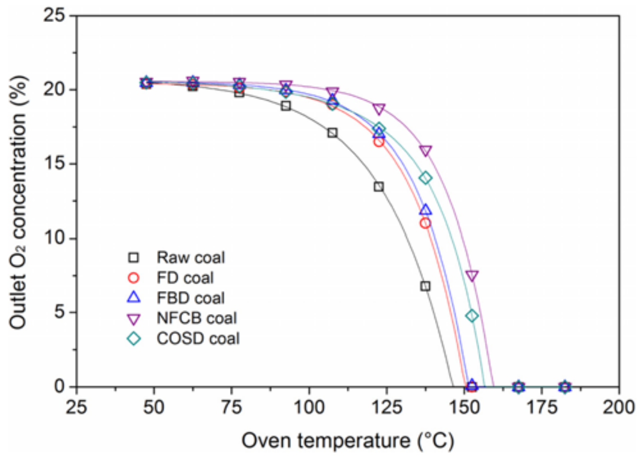

Fig. 5. Outlet concentrations of O_2 during CPT measurement.

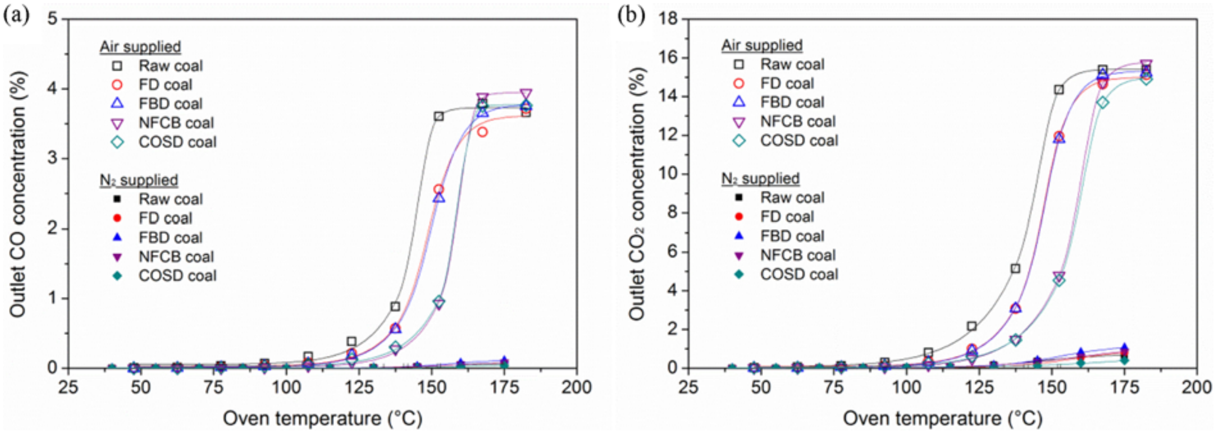

Fig. 6. Outlet concentrations of (a) CO and (b) CO_2 during CPT measurement.

as the number of oxygen functional groups on the surface of the coal decreased by the drying process, the spontaneous combustion property of the dried coal decreased by that same amount as well.

5. Gas Measurement

The results of the gas measurement show only the measurement of samples in which the CPT was close to the mean value. Fig. 5 shows the changes in O_2 concentration measured at the outlet of the vessel to which air was supplied during the CPT measurement. In all samples, the O_2 concentration at the outlet decreased slowly at the initial stage, but it decreased rapidly when the oven temperature exceeded 100-120 °C. The raw coal showed the earliest decrease in O_2 concentration, whereas the COSD coal and the NFCB coal showed the latest decrease in O_2 concentration.

Fig. 6 shows the changes in CO and CO_2 concentrations that were emitted from the vessels during the CPT measurement. In the sample to which only nitrogen was supplied, CO and CO_2 emissions increased with increases in temperature, which indicates that the thermal decomposition of coal occurs even at low temperatures, although it is a very small in quantity compared to that caused by oxidation.

Regarding the coal to which air was supplied, both the CO and CO_2 concentration began to increase rapidly when the oven temperature exceeded 130 °C. The increase in CO and CO_2 concentrations slowed at temperatures exceeding 150-160 °C because at this point, all O_2, was consumed, as shown in Fig. 5.

The raw coal showed the earliest increase in CO and CO_2 concentration, and the COSD coal and the NFCB coal showed the increases that happened the latest. An increase in CO and CO_2 concentration indicates an increase in heat generation caused by the oxidation of the coal. Thus, the earlier that CO and CO_2 was generated, the more the CPT was lowered.

The consumption of O_2 and the generation of CO and CO_2 in the dried coals were delayed because the functional groups of the dried coals, which can be involved in O_2 adsorption and oxidation, were removed in the drying process, as shown in the results of the FT-IR and XPS analysis. The reaction of coal with the oxygen occurred less during the CPT measurement. In addition, additives, such as polyethylene and asphalt, covered the surfaces of the NFCB coal and the COSD coal, and suppressed the reaction of the coal with oxygen, causing them to have the highest CPT.

CONCLUSIONS

We compared the susceptibility to spontaneous combustion of coal that was treated by different drying processes to the susceptibility of low-rank coal. Passing through the drying process, some of the oxygen functional groups were removed from the surface of the coal. In particular, this effect was notable when oil was used as the drying medium in the drying process. The more oxygen functional groups were removed from the coal, the more the O_2 adsorption and oxidation were suppressed, thus increasing the CPT of the coal. The CPTs of coals that were dried by oil were the highest among the samples. CPT is a relative measure for the estimation of susceptibility to spontaneous combustion. Therefore, based on the results of this experiment, the susceptibility to spontaneous combustion of coal can be lowered through drying processes. In particular, we found that coal dried by oil had the best suppression effect on susceptibility to spontaneous combustion. Under the condition in which coal can be used immediately after drying, the FD or FBD process would be sufficient enough for drying coal, because susceptibility to spontaneous combustion of coal can be ignored. However, under conditions where the risk of spontaneous combustion of coal is high due to transportation or storage in the open air after dying the coal, the NFCB or COSD processes would be more effective for drying the coal.

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