

Changes in spontaneous combustion characteristics of low-rank coal through pre-oxidation at low temperatures

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Abstract—This study investigated the changes in spontaneous combustion susceptibility of low-rank coal through pre-oxidation processing at low temperatures. The pre-oxidation processing on low-rank coal was conducted for a certain time at 60–150 °C in normal atmospheric conditions. The oxidation characteristics of coal at low temperature were investigated by measuring the temperature of coal and consumption of O₂ gas during the pre-oxidation processing. Physical properties of coal and changes in crossing-point temperature (CPT) caused by the pre-oxidation processing were also analyzed. Higher the temperature for pre-oxidation, the more consumption of O₂ gas in coal, and larger increase in temperature of the coal was observed. There were no significant changes in the weight of coal samples and calorific value in pre-oxidation processing upto 130 °C. It was found, from Fourier Transform Infrared Spectroscopy (FTIR) analysis, that the coal which underwent pre-oxidation processing upto 80 °C showed no significant difference from raw coal in terms of content. However, higher the temperature for preoxidation, larger decrease in aliphatic hydrocarbon and ether in the coal. As a result of CPT measurement, higher the temperature for pre-oxidation, greater the increase in CTP value of the coal. Therefore, it is expected to reduce the risk of spontaneous combustion susceptibility through the pre-oxidation method. From these results, it was confirmed that the spontaneous combustion susceptibility of the coal can be suppressed without a significant reduction in weight and calories through the preoxidation processing of low-rank coal under the proper conditions.

Keywords: Pre-oxidation, Low-rank Coal, Spontaneous Combustion, Crossing-point Temperature, Oxygen Consumption

INTRODUCTION

Low-rank coal is distributed worldwide and it has the advantage of being inexpensive compared to other fossil fuels. Yet, its use has been restricted due to high moisture content and low heating value. However, according to the increase in use of high-rank coal and high prices of oil, studies of upgraded low-rank coal have recently been conducted [1,2]. Among the methods to upgrade low-rank coal, many studies have been conducted focusing on removing moisture contained in low-rank coal [3-6]. If the large quantity of moisture contained in the low-rank coal is removed, the heating value of coal can be relatively increased.

Aside from high moisture content and low heating value of coal, high spontaneous combustion susceptibility is another problem for storage and transportation [7,8]. The spontaneous combustion of coal can occur by the reaction between coal and oxygen even at low temperature [9-11]. If the coal has an irreversible exothermic reaction to the oxygen, heat is generated. Then, if the heat of oxidation that was generated is accumulated, spontaneous combustion is promoted [12]. Spontaneous combustion of the coal may cause a fire and loss of fuels in the industrial field [13]. Therefore, the spontaneous combustion of the low-rank coal has been studied [14-17].

Especially, low-rank coal with low degree of carbonization has a high risk of spontaneous combustion. The higher the rank of the coal, the lower the risk of spontaneous combustion [18] because low-rank coal contains numerous chemical functional groups that can react with oxygen.

In general, the reaction between coal and oxygen is made in three ways [19]: (1) physical adsorption of the oxygen; (2) the bond between coal and oxygen, and chemical adsorption to oxidized carbonaceous materials; and (3) oxidation that generates gaseous substances such as CO, CO₂, and water vapor (H₂O) by the reaction between coal and oxygen.

A basic solution to control spontaneous combustion of low-rank coal is to prevent reaction of oxygen functional groups (OFGs) and oxygen. Kinoshita et al. [1] coated surface of coal with heavy oil in a dry process of coal for the basic solution. After the dry process, Hulston et al. [20] reduced the surface of coal that can react with oxygen through briquetting. Therefore, these methods involve increasing the cost for addition of processes.

However, coal is dried below a combustion temperature of coal in the dry process of coal. In this condition, if OFGs react with a regulated amount of oxygen, they would be oxidized and removed as much as the regulated amount of oxygen. It means that a reactivity with oxygen at the surface of coal decreases, so spontaneous combustion decreases, and this is a basic meaning of pre-oxidation. Heating value would be decreased in the case of pre-oxidation process. If decrease in worth of heating value through pre-oxidation is less than a value of increasing cost through the addition of pro-

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cess, an application of the pre-oxidation through the restriction method of the spontaneous combustion could be more effective.

Wang et al. [13] depicted the methods of characterizing spontaneous combustion susceptibility of coal at bulk level. Among the methods, the CPT method was widely used to characterize the susceptibility of spontaneous combustion of coal by its easiness and simplicity [18].

We investigated the effect of pre-oxidation processing of coal at low temperatures in consideration with the spontaneous combustion characteristics of coal. Pre-oxidation was conducted under 150 °C, which is below the combustion temperature of the coal. The consumption of O₂ and changes in temperature of the coal were measured during the pre-oxidation processing. Using the CPT method, we compared the spontaneous combustion characteristics among pre-oxidated coal samples and investigated the changes in chemical functional groups in the coal through FTIR analysis [21-23].

EXPERIMENTAL SETUP

1. Materials

Eco coal, which is Indonesian lignite, was used. The raw coal was ground to a 0.18-0.425 mm diameter and classified by particle size. Then it was dried for 12 hours at 107 °C under a nitrogen atmosphere.

2. Experimental Apparatus

Fig. 1 shows a schematic diagram of the apparatus used in the pre-oxidation and CPT measurement. The experimental device consists of an oven, two reactors, a gas flow controller, and a temperature data storage device. The temperature was measured with a thermocouple (TC) built in each reactor and the oven. In each reactor, a TC was inserted in a different position to measure the temperature while the reaction was taking place. Gas was supplied to each reactor passing through the copper tube coil inside the oven

to adjust the temperature.

3. Pre-oxidation Treatment

Pre-oxidation of the coal was conducted at 60 °C, 80 °C, 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, and 150 °C. After a 50 g coal sample was put into the reactor, nitrogen gas was supplied at 50 mL/min for two hours so that the temperature of the coal sample inside the reactor and the oven temperature could be set to the same temperature, 40 °C. Following this, the nitrogen was replaced with an equivalent amount of air. The temperature was increased at 10 °C/min until it reached the pre-oxidation temperature and then maintained for 5 hours. During the pre-oxidation processing, the temperature inside the oven and reactor, and O₂ concentration discharged from the reactor were measured periodically. The O₂ concentration was measured with XP 3180 of the New Cosmos Electric Co., Ltd. At the front part of the gas measurement device, a condensation trap was installed to remove moisture in the gas and to steadily maintain the temperature of the gas.

4. CPT Measurement

The CPT measurement of the coal was done as follows. After a 35 g coal sample was put into each reactor, nitrogen gas was supplied at 75 mL/min so that the temperature of the coal sample inside the reactor and the oven temperature could be equalized at 40 °C.

When the temperature of the oven and the reactor was equalized, the nitrogen was replaced with the equivalent amount of air and the temperature was raised at the rate of 0.5 °C/min until it reached 180 °C and the temperature of the oven and the reactor was monitored.

5. Analysis of Physical Properties

For the proximate analysis of the coal sample, TGA-701 of the LECO Corporation was used. For the ultimate analysis, CHN-200 (C, H, N) and SC-432DR (S) of the LECO Corporation were used. The heating value was measured with Parr 1261 from the LECO Corporation. For the FTIR analysis, Nicolet 6700 of Thermo Elec-

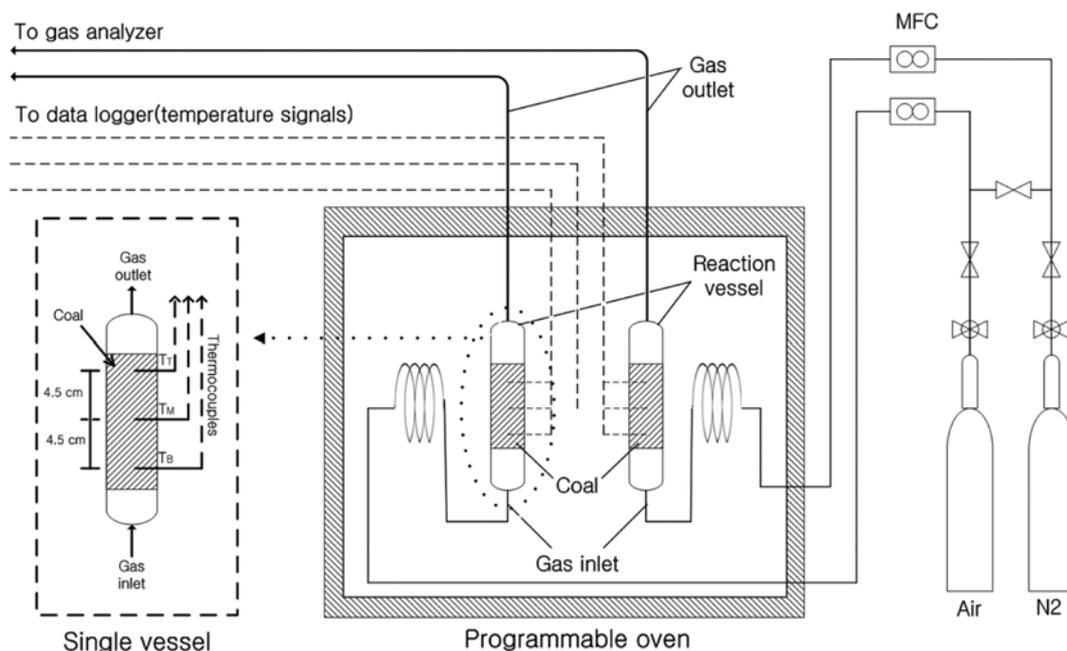


Fig. 1. Schematic diagram on pre-oxidation and CPT measurement apparatus.

Table 1. The results of proximate analysis, ultimate analysis, heating value, and changes in weight of raw coal and pre-oxidated samples

	VM	Ash (dry base)	FC	C	H	O	N	S	HHV (kJ/kg)	Weight (g)
Raw coal	54.5	4.1	41.4	67.70	5.33	21.65	1.11	0.11	26,664	50.00
Pre-oxidated at										
60 °C	52.9	3.9	43.2	67.15	5.26	22.58	1.08	0.10	26,288	50.20
80 °C	53.2	3.9	42.9	67.10	5.34	22.67	0.97	0.12	26,371	50.03
100 °C	52.3	3.9	43.8	67.45	5.29	22.42	0.98	0.12	26,664	50.38
110 °C	53.3	4.0	42.7	66.85	5.20	22.99	0.96	0.08	26,539	50.24
120 °C	53.7	4.0	42.3	67.65	5.24	22.15	0.99	0.11	26,622	50.20
130 °C	53.1	3.9	43.0	67.50	5.17	22.29	1.03	0.11	26,371	50.10
140 °C	52.3	4.2	43.5	67.60	5.15	22.04	0.96	0.11	26,329	49.44
150 °C	54.0	4.1	41.9	67.70	5.23	21.76	1.02	0.11	26,413	48.15

tron Corporation was used.

RESULTS AND DISCUSSION

1. Pre-oxidation

1-1. Physical Properties of the Pre-oxidated Coal

Table 1 shows the results of proximate analysis and ultimate analysis of coal samples, their calorific value, and weight of the coal measured after the pre-oxidation processing. As a result of proximate analysis, there was no distinct difference between raw coal and pre-oxidated coal. The measurement results of calorific value show that the calorific value of raw coal was the highest. However, the difference between the caloric values of the raw coal with that of the pre-oxidated coal samples was only 370 kJ/kg at maximum, which showed no significant difference. This was because the pre-oxidation reaction occurred at the surface of the coal and did not affect the overall physical properties of the coal much.

The weight of the coal that was pre-oxidated at or below 130 °C increased minimally compared to that of raw coal, increasing by 0.38 g at maximum. However, the weight of the coal that was pre-oxidated at or above 140 °C decreased compared to that of raw coal. In the case of processing at 150 °C, the reduction was large. It is assumed that in the case of pre-oxidation processing at or below 130 °C, the amount of coal removed by the reaction with oxygen is more than the amount of the oxygen absorbed by the coal. On the other hand, at or above 130 °C, the amount of the coal removed by the oxidation exceeds the amount of the oxygen absorbed by the coal.

From the result of ultimate analysis, the oxygen content showed a small increase compared to that of raw coal according to the increase of the temperature for pre-oxidation and then decreased. It is assumed that the oxygen in the air is absorbed by the coal physically or chemically during the pre-oxidation. However, the change in the weight of the pre-oxidated coal did not accurately coincide quantitatively to the increase in oxygen content in the ultimate analysis. It is assumed that the pre-treatment process to dry up samples again affected the result in the ultimate analysis.

As a result of analyzing physical properties of the pre-oxidated samples at low temperatures, they did not show notable difference compared to the raw coal. This is because most of the oxidation reaction which occurred at low temperatures was done on the sur-

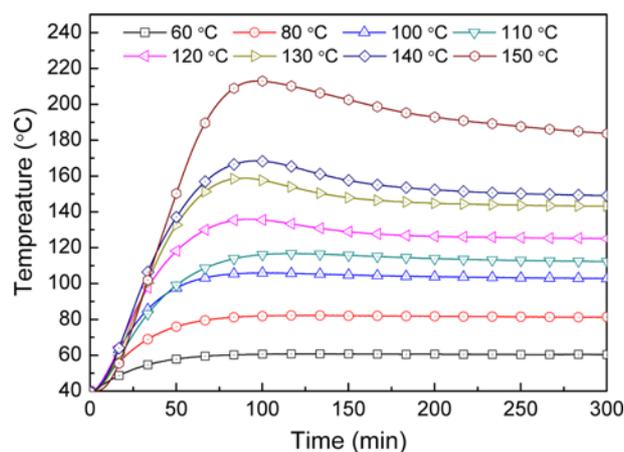


Fig. 2. Changes in the temperature of the coal at the lower part of the reactor during the pre-oxidation process.

face of the coal. However, in the case of the pre-oxidation processing at or above 140 °C, the coal weight decreased when entering into the accelerated oxidation stage in a certain position in the reactor. At the pre-oxidation processing at or below 130 °C, coal which did not enter into the accelerated oxidation stage with functional groups on the surface of the coal could be processed without any changes in physical properties and weight.

1-2. Changes in the Temperature of Coal during Pre-oxidation

Fig. 2 shows the temperature changes measured at the T_B in the lower part of the reactor based on recorded time during the pre-oxidation processing. In all cases, the temperature of the coal became higher than the temperature of the oven as time went by. This is because the heat was accumulated by the oxidation of the coal. In all reaction cases of pre-oxidation, the temperature of the coal rose as time went by, and reached its peak after approximately 70 minutes. Once the temperature peaked it fell back down and was equalized to the temperature of the oven. The higher the temperature for pre-oxidation, the larger the difference between the oven temperature and the peak value. This is because the higher the temperature gets, the more active the oxidation of the coal becomes. The temperature of the coal fell after it peaked, and we suspected the reasons were that the supplied oxygen in the air was totally con-

sumed, or the substances in the coal that could be oxidized at a given temperature had fully reacted and further oxidation could not happen.

Fig. 3 shows the temperature change according to the measurement position of the temperature inside the reactor during pre-oxidation. As shown in the Fig. 3(a), there was no difference in temperatures between the measurement points at or below 130 °C. In the case of pre-oxidation at more than 140 °C, the temperature of the coal early in the pre-oxidation process became higher at a lower

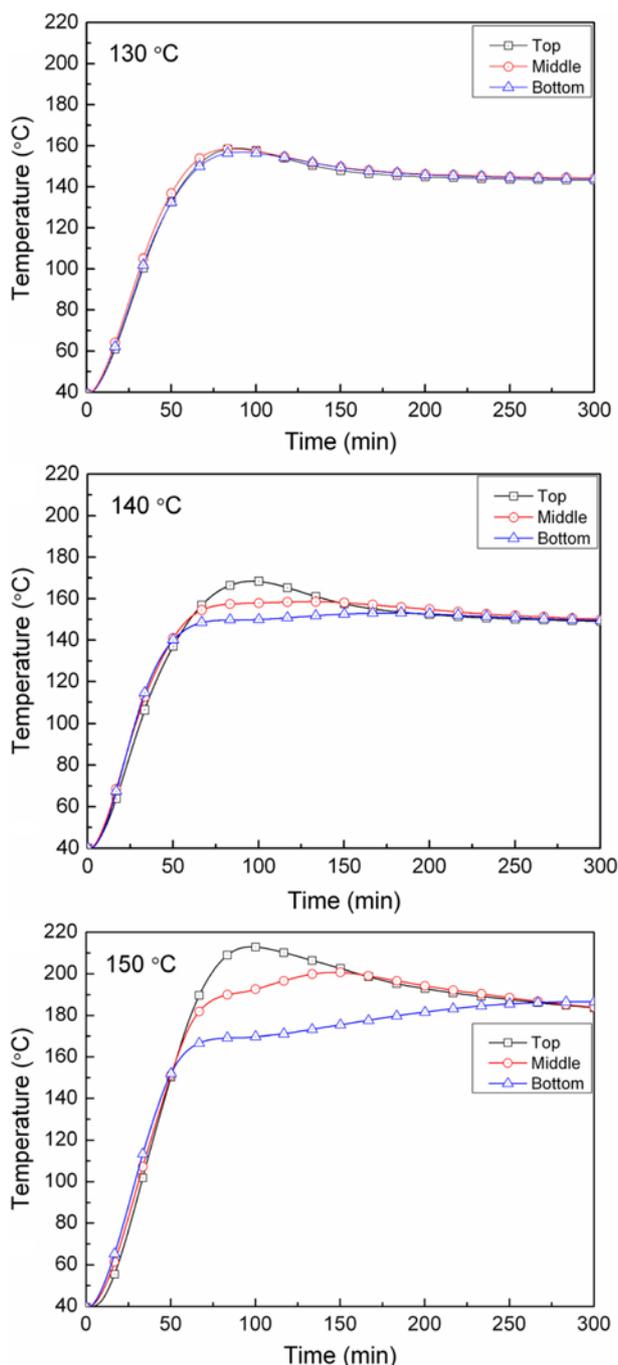


Fig. 3. Changes in temperature of the coal at upper, middle, and lower part of the reactor by temperature for pre-oxidation processing: (a) 130 °C, (b) 140 °C, (c) 150 °C.

point where fresh air was supplied and became lower at an upper point. When the temperature at the lower point dropped down after reaching the peak, the temperature at the middle point and the upper point tended to rise up. This means that in the case of pre-oxidation processing at or below 130 °C, oxidation occurred evenly in the coal at all positions inside the reactor. On the other hand, in the event of the pre-oxidation at or more than 140 °C, the oxidation occurred differently according to the position of the coal in the reactor. As the pre-oxidation temperature went up, it entered into an accelerated oxidation stage where the coal reacted to the oxygen. The accelerated oxidation stage showed notable characteristics at around 150-180 °C [9]. At this stage, aliphatic structures fell off or ruptured from the benzene rings, generating hydrocarbon gases and H_2 , while gaining energy from the generated heat of oxidation. It is known that ester species and anhydrides are formed in the coal. There, compounds work as functional groups in the active site of the oxidation reaction, which enables consecutive additional oxidation reactions.

In the event of pre-oxidation processing at 140 °C and 150 °C, the temperature peaked at approximately 80 minutes when it entered into the accelerated oxidation stage in the lower point. However, the functional groups in the active site that participate in the oxidation reaction were consumed during the pre-oxidation processing and cooled by the air flow inside, which interrupted a continuous rise of the coal temperature and made it converge to the temperature inside the oven.

1-3. Consumption of O_2 Gas during the Pre-oxidation Processing

Fig. 4 shows changes in O_2 consumption of the coal during the pre-oxidation processing. O_2 consumption was calculated based on the O_2 concentration measured in the inlet and outlet of the reactor.

Overall, the higher the temperature of pre-oxidation, the more O_2 consumption increases. This means that the higher the temperature of pre-oxidation gets, the more the coal reacts with the oxygen, which is similar to the temperature change of the coal.

When the temperature for pre-oxidation was at or below 130 °C, O_2 consumption increased at the early stage of the reaction, but decreased following that. When the air discharged from the reac-

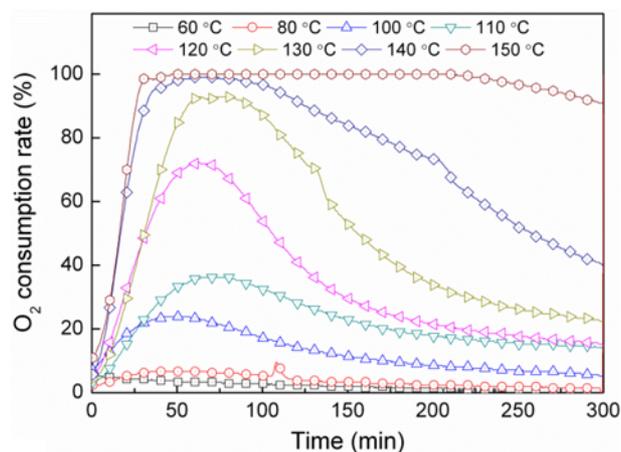


Fig. 4. Changes in O_2 consumption according to the temperature for pre-oxidation.

tor, some oxygen still remained in the reactor and O₂ consumption by the coal decreased. This means the O₂ absorption of the coal or the oxidation reaction itself decreased. The reason for the temperature drop of the coal in Fig. 2 was not because of the lack of oxygen, but because the oxygen was neither absorbed by the coal nor reacted with it at that temperature. On the other hand, when the temperature for pre-oxidation was 140 °C or 150 °C, O₂ consumption reached 100%, maintained the state for a while and then decreased. Particularly, in the case of pre-oxidation at 150 °C, O₂ consumption reached 100% and maintained the state for 220 minutes and gradually decreased after that. This means that the oxidation reaction is continuously progressing upwards to 220 minutes and then gradually decreasing after that. Since the amount of oxygen pumped into the reactor was restricted in the case of the pre-oxidation at or above 140 °C, the oxidation reaction was active in the lower part of the reactor where it contacted the fresh air. However, moving to the upper point, the oxygen concentration decreased. Thus, the oxidation reaction occurred sequentially according to the location of the coal in the reactor. The O₂ consumption reached 100% and was maintained for a certain time and decreased after that.

2. FTIR Analysis

Fig. 5 shows the FTIR analysis results of the raw coal and pre-oxidated samples in the graph. In the legend of the figure, 'POC' represents pre-oxidated coal and the numbers at the rear represent the pre-oxidated temperature. For example, 'POC60' means the pre-oxidated coal processed in the oven which was set at 60 °C.

In the case of the raw coal, the peak of aliphatic hydrocarbon and ether, which are the aliphatic functional groups, showed high values. It was because the raw coal contained a large number of active side chains, due to its low degree of carbonization.

In the figure, the spectrum of coal pre-oxidated at or below 80 °C did not show a significant difference from that of the raw coal. However, when the coal was pre-oxidated at a higher temperature, the peak decreased gradually in three distinctive parts: aliphatic hydrocarbon (C-H) of 2,900-2,800/cm and 1,450-1,350/cm, and ether (C-O-C) of 1,300-1,100/cm. In general, since low-rank coal has many active side chains, it is known to be easily dissolved or oxi-

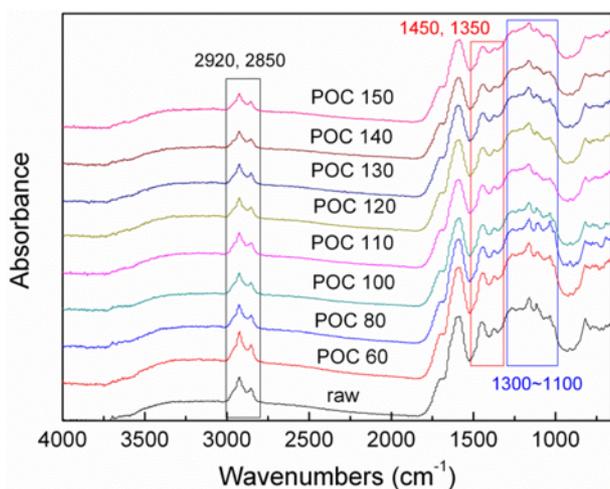


Fig. 5. FTIR analysis on raw coal and pre-oxidated samples.

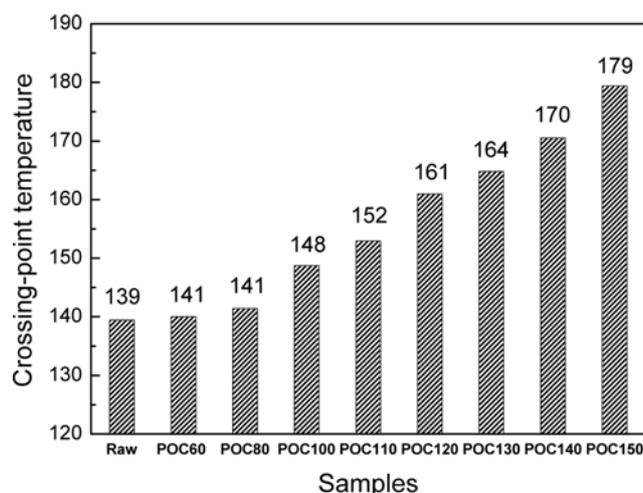


Fig. 6. CPT measurement results of raw coal and pre-oxidated samples.

dated [9]. The aliphatic hydrocarbon (C-H) and ether (C-O-C), which are kinds of active side chains, react to the oxygen becoming gasified to be the CO, CO₂, H₂O, etc., and are thus removed. The reactivity of the active side chains and the oxygen becomes better when the temperature increases. Thus, the higher the pre-oxidation temperature gets, the more product the gas generates while producing more oxygen. This explains why the rise in temperature for pre-oxidation increases O₂ consumption and generation of CO₂ gas.

3. CPT Measurement

Fig. 6 shows the results of CPT measurement on raw coal and the pre-oxidated samples. The CPT value of the raw coal was 139 °C. The CPT values of the coal pre-oxidated at high temperatures tended to get higher. The CPT values of the coal pre-oxidated at or below 80 °C did not show significant difference with that of the raw coal. On the other hand, the CPT values of the coal pre-oxidated at 150 °C showed a difference of 40 °C to that of the pre-oxidated coal, which was 179 °C. As for why the CPT value of the pre-oxidated coal showed a higher value, the substances in the coal that could react with oxygen at low temperatures were removed in advance through pre-oxidation processing, by which the reactivity of the coal with the oxygen was reduced. Therefore, by conducting pre-oxidation processing on the low-rank coal at low temperatures, the process could remove the functional groups engaged in the oxidation reaction and reduce spontaneous combustion susceptibility.

CONCLUSIONS

This study analyzed the changes in temperature, O₂ consumption, weight, and calorific value on the Eco coal, the low-rank coal, through pre-oxidation processing at 60-150 °C. We investigated the spontaneous combustion characteristics of the pre-oxidated coal.

The research result shows that there was no significant change in physical properties and weight of the coal in the case of pre-oxidation at or below 130 °C, but a small decrease in weight of the coal at or above 140 °C. As the temperature for pre-oxidation increases, aliphatic hydrocarbon and ether, which are the part of func-

tional groups of the coal, are removed through the reaction with the oxygen. This eventually results in a rise of the CPT value. That is, the spontaneous combustion susceptibility of the coal can be suppressed significantly through pre-oxidation processing.

As the temperature for pre-oxidation gets higher, the functional group is removed more actively. However, in the event of pre-oxidation processing at excessively high temperature, it may cause the loss of the coal itself and a decrease in calorific value. The range 100–130 °C is assumed to be the proper temperature for pre-oxidation under the given experimental conditions with the given samples.

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