

# Evaluation Methodology for Spontaneous Heating of Coal

～Development of low-rank coal utilization technology～

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## Abstract

The abundance of low-rank coals (sub-bituminous coals and brown coals) means they are expected to be widely used in the future. Unfortunately, the tendency of these coals to undergo spontaneous heating makes long-distance transportation and long-term storage impossible. This spontaneous heating is caused by oxidation of the coal. While considerable research on the spontaneous heating of coal has been published in the past, the complexity of the reactions involved means that the detailed mechanism has yet to be clarified. This paper describes a study aimed at finding ways to suppress spontaneous heating in coal that investigated the mechanism of spontaneous heating using simulation analysis and test methods such as TG-DSC. The mechanism of coal spontaneous heating and the evaluation methodology are discussed.

## 1 Introduction

Because low-rank coals (including sub-bituminous and brown coals) make up such a large proportion of coal reserves, use of this resource is expected to continue in the future. Unfortunately, a major problem with low-rank coals is that, being highly prone to spontaneous heating, they cannot be transported over long distances or stored for long periods of time. As a result, with the exception of certain low-rank coals, their current use is largely limited to locations close to the site of mining. The spontaneous heating in coal occurs due to the slow exothermic reaction of coal with the oxygen in air, and can ultimately result in the coal catching fire. It is a problem for the storage and transportation of low-rank coals in particular. While the phenomenon is believed to be a result of the heat given off by oxidation of the aliphatic hydrocarbons and oxygen-containing functional groups present in coal<sup>1), 2)</sup>, much about the detailed reaction mechanism remains unknown. The rate of heat generation is determined by the rate of oxidation by the oxygen in the coal and the enthalpy of the oxidation reaction. Along with the extent of oxidation and coal characteristics such as degree of coalification, moisture content, coal particle size, and mineral content, the rate of oxidation is also influenced by a large number of other factors such as the temperature and humidity at which the coal comes into contact with the atmosphere at different locations in the coal stack. Given that coal with a high oxygen content is known to be more prone to heating, the expectation that greater use will be made of low-rank coals with a high oxygen content in the future means that the problem of spontaneous heating is anticipated to grow in severity. Considerable past research has been published on this subject. Unfortunately, the complexity of the spontaneous heating reactions means that much about the detailed reaction mechanism remains unknown. Accordingly, the development of techniques for the effective utilization of low-rank coals will require elucidation of the oxidation reaction mechanism and study into ways of preventing their spontaneous heating.

This paper reviews past research into reaction mechanisms for the spontaneous heating of coal and

describes an investigation into how to assess the likelihood of coal undergoing spontaneous heating that included simulation analysis and TG-DSC testing.

## 2 Past Research into Spontaneous Heating of Coal

### 2.1 Factors involved in temperature rise in coal

This section reviews past research into the spontaneous heating of coal. Assessing the likelihood of spontaneous heating is made difficult by the fact that hydrocarbons like coal and biomass do not have a consistent composition, being a mixture of different types of combustible substances<sup>1), 2)</sup>. Wood chips, for example, have the potential to undergo fermentation by living organisms, but this possibility has been omitted from this study which is focused on coal.

The spontaneous heating of stored coal can be considered as follows. First, heating occurs on a small scale in the interior of coal stockpiles. If the quantity of coal in the pile is low, the heat is lost more quickly than it is accumulated and therefore no increase in temperature inside the pile is observed.

When large amounts of coal are stockpiled as in a coal yard, on the other hand, the heat loss from the coal pile is insufficient and the internal temperature slowly increases. When this increase reaches the ignition temperature for coal, spontaneous combustion occurs.

As identified by Miura<sup>3)</sup>, the main factors involved in the spontaneous heating of coal are believed to be the heat of adsorption resulting from water being adsorbed into the coal and the temperature rise due to oxidation reactions in the coal. Some examples from the literature that refer to these phenomena are given here. In a series of papers describing a detailed study of brown coal from Victoria, Australia conducted by that country's Commonwealth Scientific and Industrial Research Organisation (CSIRO) that considered the heat of adsorption due to the adsorption of water by brown coal after drying as well as oxidation reactions<sup>4), 5)</sup>, the phenomena were explained

using the example of brown coal from Victoria that had been dried and formed into briquettes and kept in storage. These brown coal briquettes were stored in bunkers or stockpiled in a yard and also contained coal dust that had formed during transportation. This dust from the briquettes needs to be taken into account when considering oxidation reactions. This is because dust has a very large specific surface area, meaning the oxidation reaction rate is fast. The equilibrium moisture content of the briquette is about 13 to 15% depending on atmospheric conditions. One reported instance from Victoria of a fire resulting from spontaneous heating occurred in a 7-m-high oblong pile of roughly 7,000 t of briquettes<sup>5)</sup>. An investigation of this instance of a stockpile spontaneous combustion found that it happened when rain followed an extended period of dry weather, with ignition occurring near the interface between briquettes and dust approximately 2 m from the top of the pile. Mackay<sup>6)</sup> reports that, anecdotally, spontaneous heating of brown coal briquette occurs most frequently at times of the year when the moisture content of a stockpile rises due to rainfall after an extended dry spell, also reporting that the same thing has occurred for other coal grades. This indicates that the heat generated by the adsorption of moisture (such as when rain falls on coal that has dried out) is among the causes of spontaneous heating.

Figure 1 shows a proposed reaction scheme for the oxidation of coal resulting in temperature rise<sup>7), 8)</sup>.

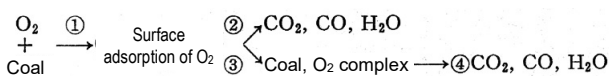


Figure 1 Coal oxidation reaction scheme at ambient temperature

It is known that, among the different reactions for the oxidation of coal at ambient temperature, reaction [1] is much faster than reactions [2] and [3]<sup>7), 8), 9)</sup>. Roughly half of the adsorbed oxygen (O<sub>2</sub>) in reactions [2] and [3] in Figure 1 remains in the coal, while the remaining half dissipates as gas. It is also believed that the amount of oxygen adsorbed as a result of reactions [2] and [3] depends on the coal grade (chemical structure) and reaction conditions. It has been noted that low-rank coals (coals with a low degree of coalification) typically have

faster oxidation reaction rates than other coal grades<sup>8)</sup>. The factors (reaction conditions) that influence the reaction rate for the oxidation of coal at ambient temperature are the temperature of incoming air, concentration of oxygen, rate of temperature increase, and coal particle size (specific surface area).

## 2.2 Models of coal structure

To investigate the spontaneous heating of coal, it is important to understand its chemical structure. Figures 2 to 4 show example models for the structure of brown coal and bituminous coal.

Figure 2 shows the model for the structure of German brown coal published by Hüttinger et al<sup>10)</sup>. This model presents the structure of brown coal with one to three aromatic rings that are linked to aldehyde (-CHO), carboxy (-COOH), and other oxygen-containing functional groups, and to methyl groups (CH<sub>3</sub>) and other aliphatic hydrocarbons. Here, the structure of brown coal includes long chains and branched chains of aromatic carbon with metal cations attached by ionic bonds to the carboxy groups.

Kumagai et al<sup>11)</sup> used the results of NMR and other structural analyses to study models of the structure of brown coal and proposed the unit structure model shown in Figure 3. As with Hüttinger et al, this model also proposes a unit structure for brown coal based on aromatic rings together with oxygen-containing functional groups and aliphatic hydrocarbons.

Figure 4 shows a model for the structure of Illinois No. 6, a bituminous coal from the USA, that was proposed by Shinn<sup>12)</sup>. Comparing this model for bituminous coal to the brown coal models in Figures 2 and 3 indicates the following. The circled elements in the coal structure models of Figures 2 to 4 are aliphatic hydrocarbons (branched chains) and oxygen-containing functional groups. Being a bituminous coal with a higher degree of coalification than brown coal, aromatic rings are more prominent in Illinois No. 6 while the proportion of aliphatic hydrocarbons (-CH<sub>3</sub>) is low. Furthermore, carboxy (-COOH) and aldehyde (-CHO) oxygen-containing functional groups are largely absent.

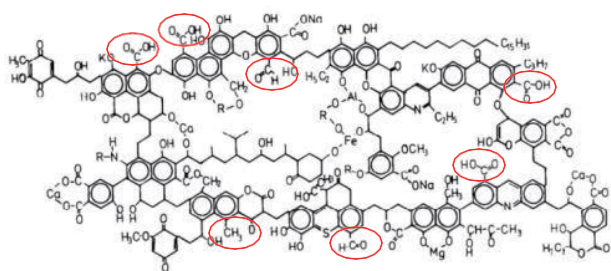


Figure 2 Brown coal structure model (K. J. Hüttinger, 1987)

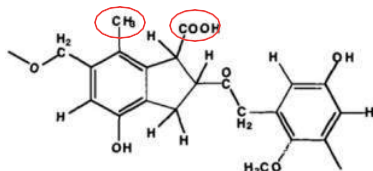


Figure 3 Unit structure assumed for LY model molecule (H Kumagai, 1999)

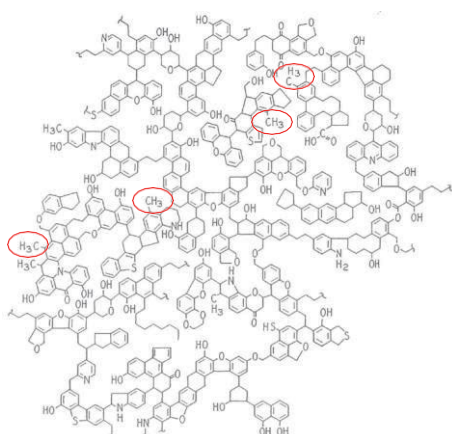


Figure 4 Bituminous coal structure model (J. H. Shinn, 1984)

To summarize, the structure of brown coal is characterized by having a higher proportion of aliphatic hydrocarbons (branched chains) and oxygen-containing functional groups in its unit structure than is the case for bituminous coal.

Section 3 describes an investigation into the mechanisms and different spontaneous heating characteristics resulting from the differences between these coals.

### 2.3 Reaction mechanism for coal oxidation

While considerable research has been done on the reaction mechanism for coal oxidation, much of the details remain unknown. This is due to the complexity of the reaction, with oxidation involving a number of different reactions occurring simultaneously. For the reaction mechanism for

coal oxidation in an oxidizing atmosphere, Miura et al<sup>1), 2)</sup> proposed the model of coal structural change shown in Figure 5. The oxidation of the aliphatic hydrocarbons (-CH<sub>3</sub>) present in the chemical structure of coal results in the formation of peroxides (-CH<sub>2</sub>-OOH) at temperatures up to 140 °C, carboxy groups (-COOH) by the loss of CO<sub>2</sub> and H<sub>2</sub>O at 200 °C, ester groups (-COO) by the loss of CO<sub>2</sub> and H<sub>2</sub>O at 260 °C, and anhydrides (-COOCO-) by the loss of CO<sub>2</sub> and H<sub>2</sub>O at 300 °C. Furthermore, oxidation of the central aromatic ring structure occurs when temperatures exceed 360 °C, resulting in the formation of H<sub>2</sub>O, CO<sub>2</sub>, and CO.

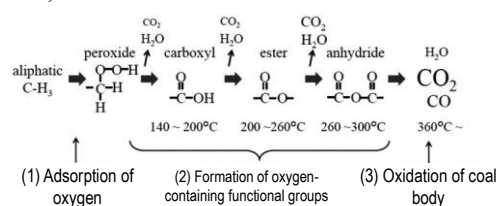


Figure 5 Coal structural change caused by oxidation reaction

Accordingly, section 3 will describe the use of quantum chemical calculations (molecular simulation) to investigate the mechanism of heat generation by oxidation of the aliphatic hydrocarbons and oxygen-containing functional groups present in the structure of coal.

## 3 Analysis of Spontaneous Heating Reactions in Coal by Quantum Chemical Calculation

### 3.1 Analysis method

Quantum chemical calculations that simulated reactions at a molecular level were used to analyze the stability of spontaneous heating reactions involving the aliphatic hydrocarbons and oxygen-containing functional groups present in the structure of coal (low-temperature oxidation reactions) in terms of the reaction pathways and energy levels.

The calculation involved using B3LYP, a method based on density functional theory, to calculate the energy levels at which stable structures reach their optimal structures. The Gaussian09 program was used for the calculation, with 6-31G\* as the basis functions.

The oxidation reaction mechanism for the spontaneous heating of coal was based on the model for the oxidation of aliphatic hydrocarbons and oxygen-containing functional groups proposed by Miura et al<sup>1), 2)</sup> and shown in Figure 5. Use of the Figures 2 to 4 models in the simplified structure model of coal for the quantum chemical calculation was considered and this led to the adoption of the structure model made up of a central aromatic ring structure with aliphatic hydrocarbon (-CH<sub>3</sub>) branches shown in Figure 6. The coal structure model in Figure 6 assumes a basic structure made up of a single aromatic ring (benzene ring) to which methyl groups are attached<sup>1)</sup>. This was used to investigate the oxidation of aliphatic hydrocarbons (methyl groups), which represents the initial stage of the oxidation reaction associated with spontaneous heating. That is, of the aliphatic hydrocarbons present, it is the methyl groups in a benzylic position (adjacent to the benzene ring) that are highly reactive and likely to be involved in an oxidation reaction.

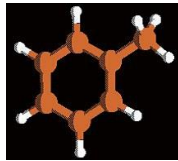


Figure 6 Simplified coal structure model

It was assumed that the oxidation reaction involves molecular oxygen and that the oxidation sequence is: Methyl groups (-CH<sub>3</sub>) → peroxides (-CH<sub>2</sub>OOH) → aldehydes (-CHO) → carboxy (-COOH) → esters (-COOR), anhydrides (-COOCOR).

### 3.2 Analysis results and commentary

Figure 7 shows an example of the oxidation reaction calculation (methyl group → peroxide). The analysis optimizes the structure of each molecule and calculates the energies of these optimized structures to determine the energy difference between reactants and product. For the Figure 7 reaction, transformation of the methyl groups attached to the aromatic ring (benzene ring) into peroxide results in an energy difference of -10.5 kcal/mol.

This means that the energy of the product when it reaches a stable structure is 10.5 kcal/mol less than the energy prior to the reaction (in other words, an exothermic reaction).

	reactant		product
PASS 1	Coal-CH <sub>3</sub>	O <sub>2</sub>	Coal peroxide
E (kcal/mol)	0.0		-10.5

Figure 7 Coal oxidation reaction model

Figure 8 shows the optimized structure and energy level obtained by the quantum chemical calculation for each molecule. Assuming a reaction pathway based on the oxidation reaction model (Figure 5) of Miura et al<sup>1), 2)</sup>, the oxidation sequence starts with the aliphatic hydrocarbons present in the coal, specifically the methyl groups. The sequence is: methyl groups (-CH<sub>3</sub>) → peroxides (-CH<sub>2</sub>OOH) → aldehydes (-CHO) → carboxy (-COOH) → esters (-COOR), and anhydrides (-COOCOR). The energy levels are obtained by comparing the energies of the reactants and products. A reaction is endothermic if the products have more energy than the reactants and exothermic if they have less energy. The results of using the quantum chemical calculation to analyze the oxidation reaction pathway for spontaneous heating indicate that the reaction pathway is appropriate with no unstable intermediate products. Also, most of the oxidation reactions are exothermic, meaning that the temperature of the coal will rise if the amount of heat generated exceeds the amount dissipated.

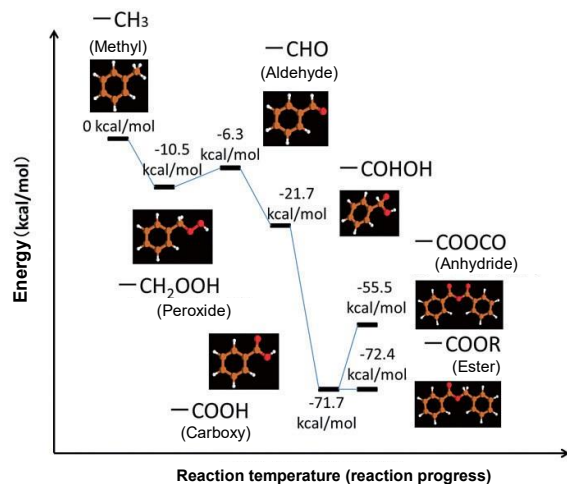


Figure 8 Optimized structure and energy level of each molecule

## 4 Evaluation of How Likelihood of Spontaneous Heating Varies for Different Types of Coal

Thermal analysis is commonly used to assess how likely coal is to undergo spontaneous heating. Test equipment for measuring heat include thermogravimetric (TG) analyzers, differential analyzers (DTAs), and differential scanning calorimeters (DSCs). As these test methods are able to measure the thermal characteristics of samples quickly, they are designated as test methods for hazard assessment in Japan's Fire Service Act<sup>13</sup>. The wire basket test for self-heating specified in the United Nations Recommendations on the Transport of Dangerous Goods is also widely used<sup>14</sup>.

The two methods used in this study were the measurement of heat generation (DSC test) and the wire basket test.

### 4.1 Coal samples

Table 1 lists the proximate analysis and ultimate analysis results for the coal samples used in testing along with their higher heating value (HHV). A comparison of the degree of coalification indicates that sub-bituminous coal A has a lower carbon (C) content, higher oxygen (O) content, and lower degree of coalification than bituminous coal B and bituminous coal C, as can be seen in Table 1. As noted in section 2.2, sub-bituminous coal A has a smaller amount of aromatic hydrocarbon in its central structure than do bituminous coal B and bituminous coal C. It also has more aliphatic hydrocarbon and oxygen-containing functional groups, allowing for more oxidation reactions in the low temperature range.

Table 1 Properties of coal samples

	Proximate analysis				Ultimate analysis					Calorific value
	Total moisture	Ash	Volatiles	Fixed carbon	C	H	N	O	S	HHV [measured]
	mass %	mass%-dry			mass%-daf					kJ/kg-dry
Sub-bituminous coal Dried coal A	4.6	4.2	46.0	49.9	71.6	5.1	1.1	22.0	0.2	28042
Bituminous coal Coal B	12.1	13.5	33.1	53.4	81.3	5.0	2.1	10.9	0.6	29461
Bituminous coal Coal C	11.3	11.4	35.8	52.7	78.6	5.3	1.0	14.8	0.3	29473

### 4.2 Measurement of heat generation

A TG-DSC analyzer (NETZSCH STA449F3) for thermogravimetric analysis and scanning calorimetry was used to study the generation of heat during oxidation reactions at an ambient temperature of 107 °C and in an air atmosphere, and to assess how heat generation in the low temperature range differed between the different types of coal. The coal was crushed to a particle size of 210 µm or less and weighed out into 12-mg samples. After heating to 107 °C at a rate of 3 °C/min in a nitrogen atmosphere (nitrogen flow rate of 100 mL/min), the samples were switched from a nitrogen to an air atmosphere (air flow rate of 100 mL/min) and held for one hour before measuring heat generation.

Figure 9 shows the test results. The horizontal axis represents the elapsed time after the coal samples reached 107 °C and were switched to an air atmosphere, while the vertical axis represents the cumulative heat generated by the oxidation reaction. Larger values on the vertical axis indicate that the coal generated more heat. From Figure 9, it can be seen that the amount of heat generated by the sub-bituminous coal (coal A) was greater than that generated by the bituminous coal (coal B).

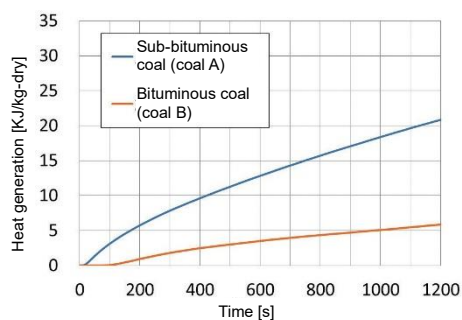


Figure 9 Heat generation by coal oxidation reactions

### 4.3 Wire basket test

The heat generation measurements described in section 4.2 were conducted on small samples (about 10 mg) and used to determine things like whether or not the samples themselves were heat-producing. Assessing the potential for spontaneous heating in coal needs to determine this while also considering the balance between the generation and loss of heat in a pile of coal. For this purpose, the wire basket test is used to assess the potential for spontaneous

heating in coal samples of about 1 kg. The test method used to assess spontaneous heating involves a cubic wire basket (10 cm per side with a volume of 1 l) into which is placed a sample of about 700 g of coal crushed to 10 mm or smaller particles. This is then placed in a constant-temperature chamber at 140 °C and held at this temperature while the internal temperature of the coal sample is recorded to determine how it changes over time and how long it takes to reach 200 °C.

Figure 10 shows the results for a wire basket test. These show that sub-bituminous coal A reaches 200 °C more quickly than bituminous coal C, meaning that spontaneous combustion will occur sooner for coal A and that it has a greater potential for spontaneous heating.

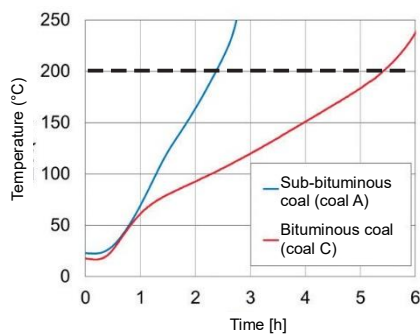


Figure 10 Wire basket experimental results

These results provide the following conclusions. Sub-bituminous coal has a greater potential for spontaneous heating than bituminous coal. This result indicates that sub-bituminous coal with its high proportion of aliphatic hydrocarbons and oxygen-containing functional groups generates more heat at low temperatures and has greater potential for spontaneous heating than bituminous coal, supporting the results of the heat generation analysis performed using the quantum chemical calculation. (Future tasks)

The intention is to investigate techniques for assessing spontaneous heating in a wider range of coal grades. Also, given that the lignin that forms the core structure in woody biomass is made up of single aromatic rings to which aliphatic hydrocarbons, oxygen-containing functional groups, and other groups are attached<sup>15), 16)</sup>, there is potential for extending the use of the quantum chemical calculation and spontaneous heating test methods

proposed in this paper to this and other solid hydrocarbon materials. The intention is to investigate the scope of application of these methods more widely in the future.

## 5 Conclusion

Methods for analyzing the reaction mechanism were investigated with the aim of conducting a study into how to prevent the spontaneous heating of coal. Using these results, a quantum chemical calculation based on the assumed oxidation reaction mechanism for coal was performed and a reaction scheme proposed for the oxidation that occurs in spontaneous heating involving the aliphatic hydrocarbons and oxygen-containing functional groups that form part of the chemical structure of coal. The respective spontaneous heating characteristics of bituminous and sub-bituminous coals were also considered, these being different types of coal with different degrees of coalification.

It is believed that the techniques proposed in this paper for assessing spontaneous heating also have potential applications with other hydrocarbons such as woody biomass. The intention is to look at extending the application of these methods so that they can be used for assessing the likelihood of spontaneous heating based on coal grade and in materials such as woody biomass that are structurally similar to brown coal and other coals.

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## References

- 1) Kouichi Miura, Hiroyasu Fujitsuka, "Mechanism of Spontaneous Combustion of Low-rank Coals and Methods of Suppressing Spontaneous Combustion," Journal of the Japan Institute of Energy, 93, 1054-1065 (2014) in Japanese.
  - 2) H. Fujitsuka, R. Ashida, M. Kawase, K. Miura, *Energy Fuels*, 28, 2402-2407 (2014)
  - 3) Kouichi Miura, Journal of the Japan Institute of Energy, 94, 1169-1172 (2015) in Japanese.
  - 4) Ed. By R. A. Durie, "*The Science of Victorian Brown Coal-Structure, Properties, and Consequences for Utilisation*," Butterworth Heinemann, (1991)
  - 5) M. F. R. Mulcahy, W. J. Morley and I. W. Smith, "*The Science of Victorian Brown Coal-Structure, Properties, and Consequences for Utilisation*," Chap. 8 Combustion, gasification and Oxidation, Butterworth Heinemann, (1991)
  - 6) G. Mackay, "Spontaneous combustion behavior of brown coal briquette and solar dried slurry," SECV Research and Development Dept. Report, 50/88/47 (1988)
  - 7) Kinji Hoshizawa, Kazuo Koyata, Tetsuo Ono, Journal of the Fuel Society of Japan, vol. 64 (1985), No. 4, pp. 224-239 in Japanese.
  - 8) Motoya Nakamura, Takashi Kiga, Katsumi Takahashi, and Kohei Suzuki, Ishikawajima-Harima Engineering Review, vol. 36, No. 3 (1996), pp. 208-212 in Japanese.
  - 9) Katsumi Takahashi, Hiroyuki Uchida, Takashi Watanabe, Kazumasa Takahashi, Ishikawajima-Harima Engineering Review, vol. 23, No. 5 (1996), pp. 439-444 in Japanese.
  - 10) K. J. Hüttinger, and A. W. Micchnfelder, *Fuel*, 66 (1987), p. 1164-1165
  - 11) H. Kumagai, T. Chiba, K. Nakamura: ACS, Div. of Fuel Chemistry, (1999), pp. 633-636
  - 12) J. H. Shinn, *Fuel*, 63(1984), pp. 1187-1196
  - 13) Proceedings of the 11th Annual Research Conference of the National Research Institute of Fire and Disaster, 2008, p. 11 in Japanese.
  - 14) Research Report of Fire Research Laboratory, Fire Research Laboratory, Vol. 58, 2003, pp. 12-14 in Japanese.
  - 15) H. Nimz, *Angewandte Chemie International Edition*, 74 (1974), pp. 313-321
  - 16) E. Salmon, F. Behar, F. Lorant, P. M. Marquaire, *Organic Geochemistry*, 40 (2000), pp. 500-509
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