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Title	Evaluation Methods of Coking Coal for Coke Manufacturing : Hydrogen and Electron Transfer Abilities of Coal
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Citation	北海道大學工學部研究報告, 162, 29-36
Issue Date	1993-01-29
Doc URL	https://hdl.handle.net/2115/42346
Type	departmental bulletin paper
File Information	162_29-36.pdf

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北海道大学工学部研究報告
第162号（平成4年）

Bulletin of the Faculty of Engineering
Hokkaido University, No. 162 (1992)

Evaluation Methods of Coking Coal for Coke Manufacturing
—Hydrogen and Electron Transfer Abilities of Coal—

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(Received September 18, 1992)

Abstract

Evaluation method for coking coal has been proposed for coke manufacturing. The distribution of optical textures in coke was evaluated by an automatic image analysis system. Hydrogen donor and acceptor abilities of coal were measured. The extent of the development of anisotropic texture in the coke is correlated closely to hydrogen transfer ability of the coal and coal blend.

Change of spin concentration as a function of charge (electron) transfer ability of iodine doped coal correlates with the maximum fluidity and temperature ranges of plastic stage of coal, respectively. The relationship between the extent of fine mosaic texture in the coke and the change of spin concentration for the iodine doped coal has been also recognized.

Hydrogen and charge (electron) transfer abilities of coal take a part of deep understanding for structure and carbonization reactivity of coal.

1. Introduction

In coke manufacturing, the blending of various coal is a practical way in order to improve coke quality such as strength, carbon dioxide reactivity and so on. It is well known that there is a good correlation between the quality and texture of coke[1]. The larger the extent of optically anisotropic texture of coke is, the higher the coke quality becomes[2,3]. So the development of anisotropic texture provides important information for design of coke making.

In current coke making for blast furnace in Japan, the mean maximum reflectance of vitrinite in oil, Ro, and maximum fluidity measured by Gieseler plastometer, MF, are adopted as dominant characteristics of single or blended coal for quality control[4]. $\bar{R}o$ is a function of development of optical texture of coal. MF is considered to reflect chemical structure of coal. However, there are no chemistry about pyrolysis and carbonization reactions governing for single and/or blended coals.

In this paper, we propose new evaluation parameters of coal, hydrogen and electron transfer abilities in order to provide reaction chemistry.

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2. Experimental

2. 1. Coal Sample and Hydrogen and Electron Transfer Abilities

Nine different coking coals were selected as samples. The elemental analysis of coals is shown in Table 1. In a part of experiments, Argonne Premium Coal Samples were also used. Analytical data of them are given in elsewhere[6].

Table 1 Elemental Analysis of Coals

Coals	Ultimate Analysis (wt%, daf)					Ash (wt%)
	C	H	N	S	O	
Oyubari	87.1	6.1	1.6	0.3	4.9	6.8
Hunter Valley	81.8	5.3	1.5	0.4	11.0	6.7
Goonyella	88.6	5.1	1.7	0.5	4.1	8.1
South Bulli	88.0	4.9	1.5	0.4	5.2	9.4
Peak Downs	89.9	5.0	1.9	0.6	2.6	8.0
Luling	87.9	5.1	1.4	0.3	5.3	10.0
Masco	86.5	5.2	1.4	0.6	6.3	7.9
Saraji	90.8	5.2	1.8	0.6	1.6	9.5
Slal Fork	91.7	4.6	1.2	1.0	1.5	5.3

It has been reported that hydrogen donor, Da, and acceptor, Aa, abilities of coal are important characteristics in the carbonization system[7]. Da and Aa of the samples were assessed by the extent of hydrogen transferred during heating with anthracene as a hydrogen acceptor and with 9.10-dihydroanthracene as a hydrogen donor, respectively. Detail procedure and calculation methods of Da and Aa were described in elsewhere[7,8]. Da ($mg \cdot H_2/g \cdot$ coal) means the extent of transferable hydrogen in coal molecules. The transferable hydrogen stabilize the sites of free radical and functional group at pyrolysis temperature (400°C) in the reaction system. Aa ($mg \cdot H_2/g \cdot$coal), on the other hand, is hydrogen capping ability due to free radicals, functional groups and other reactive sites at pyrolysis temperature.

Coal molecules interact as host with selected electron acceptors as guest molecules, when they are mixing. We choose iodine as a guest molecule in this experiment. Here, we propose the electron transfer ability expressed by of change of spin concentration in the sample. Measurements are done at room temperature by electron spin resonance spectroscopy. That is, the spin concentration of coal changes with and without the guest molecule. Nso, and Ns are the values of spin concentration of coal before and after 10% iodine addition, respectively.

2. 2. Optical Texture Measurement

It has been developed an automatic system for measuring the optical texture of coke[5]. In this system microscopic images of the textures are taken by a TV camera and processed by a CPU, which identifies the patterns of texture based on image analysis techniques. With the support of autofocusing unit, the operator-free measuring has been established. The texture distribution data is precise, reproducible and free from difference of individuals.

Coke prepared and supplied from Osaka Gas Co. was molded and polished as usual, and optical textures were examined by automatic measuring system[5]. Table 2 shows the texture classification used in this investigation.

Table 2 Classification of Optical Texture in Coke

Description of Optical Texture	Size
Isotropic Texture	No optical activity
Fines Mosaic Texture	Grain size $<1.5\,\mu$
Coarse Mosaic Texture	$1.5\,\mu >$ grain size $> 10\,\mu$
Leaflet Texture	$10\,\mu <$ width in flow pattern
Inert Texture	Texture derived from inert macerals in coal

3. Results and Discussion

3.1. Coking Characteristics of Coal

As described above, $\bar{R}o$ is one of fundamental characteristics of coking coal. Relation between maximum fluidity, MF, and $\bar{R}o$ is a key map for evaluation of coking coal[4]. Figure 1 presents the relationships between (a) MF, (b) resolidification temperature, T_S, and (c) temperature at MF, T_M, and $\bar{R}o$ for the coal samples used here, respectively. Clear correlations of MF and T_S with rank are recognized for the samples from Figure 1. MF and Ts give a maximum at the $\bar{R}o$ value of 1.0-1.5. Temperature at maximum fluidity, T_M, increases also with increase of coal rank as shown in Figure 1.

In order to get deep understanding of the changes in molecular level during coking, we have attempted to obtain the relationship of $\bar{R}o$ versus hydrogen or electron transfer ability of coal. Figure 2 shows the relations between hydrogen transfer ability, Da/Aa, or electron transfer one, Ns-Nso, and $\bar{R}o$, respectively, where Da/Aa is the ratio of hydrogen donor and acceptor abilities and Ns-Nso is relevant to electron transfer ability of coal molecule. It is clearly recognized from Figure 2 that Da/Aa and Ns-Nso increase with the increase of $\bar{R}o$, reach a maximum in the vicinity of $\bar{R}o$= 1.0 and then decrease.

Following figures show the correlations of Da/Aa versus coking characteristics. Figure 3 illustrates the relationship between those characteristic parameters and Da/Aa. Temperature range of plastic stage, $\triangle T$, MF and T_S were obtained from Gieseler plastometry.

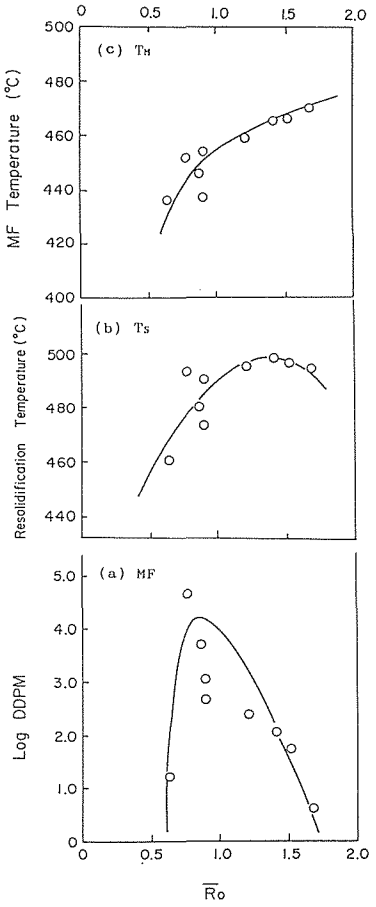

Fig. 1 Relations between characteristics obtained by Gieseler plastomery and maximum mean reflectance of coal

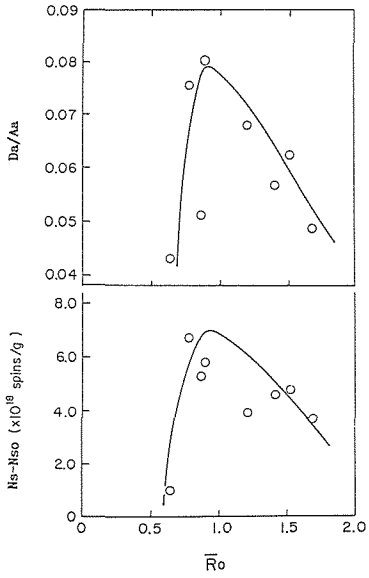

Fig. 2 Relations between hydrogen and electron donor abilities and maximum mean reflectance of coal

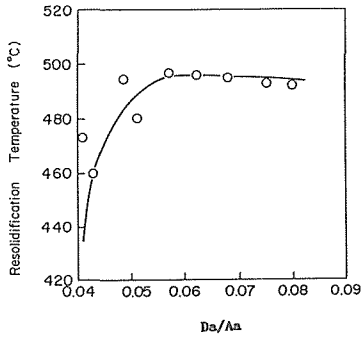

Fig. 4 Relation between resolidification temperature and hydrogen donor ability of coal

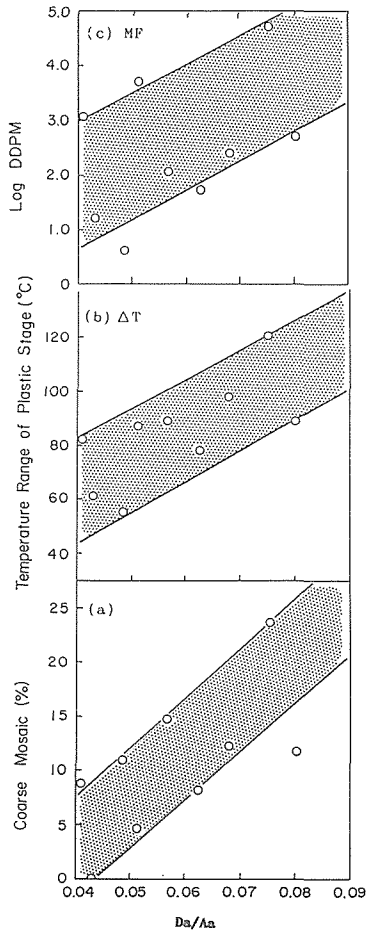

Fig. 3 Changes of characteristics obtained by Gieseler plastometry and optical texture versus hydrogen donor ability of coal

The content of coarse mosaic texture in coke was obtained by automatic optical texture analysis. The parameters as shown in Figure 3 seem to be as a function of Da/Aa, but plots spread in a wide band. On the other hand, resolidification temperature of the coals, T_S, is closely correlating with Da/Aa as shown in Figure 4.

The possible reaction paths of transferable hydrogen, H*, in the reaction system are considered as follows ; (1) stabilization of thermally induced reactive free radicals, (2) consumption by oxygenated functional groups within coals and (3) hydrogenation of aromatic carbon atoms with high electron density[11]. All the reaction paths help (1) keeping at low viscosity at pyrolysis temperature and (2) rearrangement and parallel stacking of aromatic

flat molecules in coal during plastic stage. Therefore, the development of anisotropic texture in the resultant coke is a function of the extent of hydrogen transfered[8, 11].

In order to interpret the role and potential of hydrogen transfer in the co-carbonization system of coal with coal tar pitch, we introduce a parameter D/A. This is defined by equation (1),

$$D/A = \frac{m_1(Da)\,pitch + m_2(Da)\,coal}{m_2(Aa)\,coal} \quad (1)$$

where m_1, and m_2 mean the percent by weight of pitch and coal, respectively. The numerator means the total extent of donable hydrogen, while the dominator denotes the extent of hydrogen acceptability of coal species. Acceptability of hydrogen by pitch molecules neglected, because acceptability of the coal molecules and/or moieties formed during pyrolysis is larger than that of pitch molecules.

Figure 5(a) illustrates the relationship between D/A and C% for coal and coal tar pitch mixtures. Plots for each line are corresponding to the mixture, in which pitch content varies over the ranges from 0, 10, 20 to 40%, respectively. Good correlation is obtained between the value of D/A and C% for a given coal-tar pitch mixture.

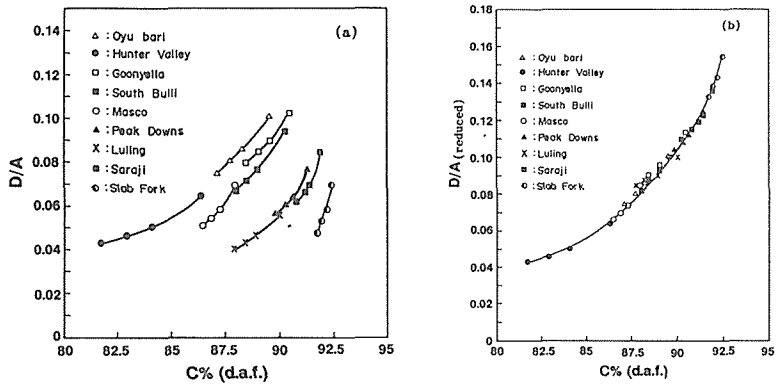

Fig. 5 Relation between (a)D/A and C% of blend, and (b)$D/A_{reduced}$ and C% of blend

In order to get a curve (master curve), vertical shift has been done for each D/A - C% line of the coal-coal tar pitch systems in figure 5(b). Hunter Valley Coal is chosen as a reference in this case. Namely, the curve of D/A - C% of Hunter Valley Coal is fixed. After operation of vertical shift, we can get a smooth master curve of D/A - C%. The resultant master curve of $D/A_{reduced}$ versus C% is illustrated in Figure 5(b). Hypothetical hydrogen transfer ability for the given coal is deduced from the master curve in Figure 5(b). The value of $D/A_{reduced}$ is one of characterization parameters relevant to hydrogen transfer. Shift factors are summarized in Table 3.

Transferable hydrogen in coal is responsible for the development of optical texture in resultant coke[7, 8]. Therefore, it is stressed that $D/A_{reduced}$ of coal is an extent governing coking characteristics during pyrolysis of coal occurs. It is suggested that parameter relevant to optically anisotropic texture of coke could expressed by $D/A_{reduced}$. Let us propose here an index of optical texture of coke based upon practical coke performance such

Table 3 Da/Aa and $D/A_{reduced}$ in coal

coals	Da/Aa	$D/A_{reduced}$	shift factor*
Oyubari	.075	.075	0
Hunter Valley	.043	.043	0
Goonyella	.080	.091	.011
South Bulli	.068	.083	.015
Peak Downs	.051	.066	.015
Luling	.057	.105	.048
Masco	.041	.085	.044
Saraji	.062	.115	.053
Slab Fork	.049	.134	.085

* shift factor $=[D/A_{reduced}-D/A]$

as density, porosity, strength, reactivity and so on. The texture index, TI, are derived from following equation,

$$TI=-5(ISO)+0(FM)+0(FIB)+(CM)+5(LF)-2(INT) \quad (2)$$

where ISO, FM, FIB, CM, LF and INT are the percentage of isotropic, fine mosaic, fibrous, coarse mosaic, leaflet and intent texture, respectively. Input data are the results by optical texture measurements. In the equation (2), the coefficients are determined from regression analysis with more than hundred separate samples.

Figure 6 shows the relationship between the TI and $D/A_{reduced}$. Fairly good correlation is recognized between TI and $D/A_{reduced}$. Plot of Peakdown coal (marked as * in Figure 6) is located at far from correlation line. This is due to that this coal behaves always abnormal coking property based on its coal rank . The reason will be disclosed by further studies. The fact means that prediction of "coke" quality become possible using by the $D/A_{reduced}$ value of "coal".

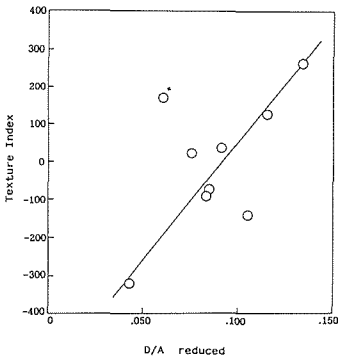

Fig. 6 Relation between texture index of coke and $D/A_{reduced}$ of coal

The degree of interaction between the host and the guest molecules gives us an information not only of non-covalent bonding, but also of coking behavior of host molecules. Figure 7 illustrates the changes of MF, $\triangle T$ of the coals and the percentage of fine mosaic texture in the resultant coke versus Ns-Nso. All properties drawn in Figure 7 increase with increase of Ns-Nso, respectively.

It has been clarified from the similar experiment for the selected polynuclear hydrocarbon compounds. The value of Ns-Nso shows the extent of size and shape of aromatic ring[10]. Strong interaction between iodine and coal molecules results formation of charge-transfer complexes[10]. For Argonne Premium Coal Samples, the value of Ns-Nso rise monotonically with increase of coal rank up to 91%C. The value of Ns-Nso for iodine doped coal decreases with increase of H/C (atomic ratio, d.a.f. basis) as a parameter of aromaticity for coal. Taking account of the facts described above, MF, $\triangle T$ and the extent

of fine mosaic texture are closely related to the electron donor ability of coal molecules. In another word, basicity of the coal molecules may govern the coking behaviors.

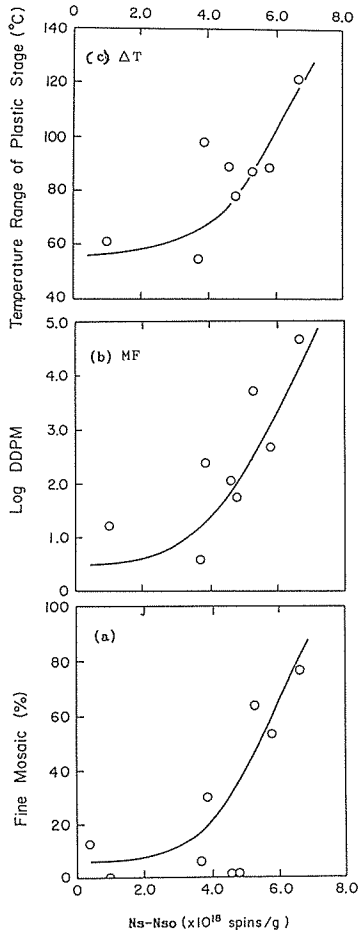

Fig. 7 Changes of characteristics by obtained Gieseler plastometry and optical texture versus electron donor ability of coal

4. Conclusion

In conclusion, hydrogen and electron transfer abilities of coal relate coking characteristics of coal. It is stressed that hydrogen and electron transfer abilities of coal are obtainalbe even in non volatile solid samples and are simple and not time-consuming methods. The measurements are applicable for not only single coal but also for blended coals. The methodologies we propose could help the design of the coal blending for coke manufacturing.

(The paper is a part of the cooperarive project between Hokkaido University and Osaka Gas Co., 1986-1987, and presented at "Third Conference of Hokkaido University and University Science and Technology Beijing, September, 1991, Beijing, China.)

References

1) Otani, S. and Sanada, Y.: Introduction to Carbonization Engineering, (1980), p. 226, Ohmu-sya.
2) Koba, K., Sakata K. and Ida, K.: J. Fuel Soc. Japan, **60** (1981), p. 333
3) Miyamura, T., Saga, M. and Tanihara, H.: Fuel Soc. Japan, **56** (1977), p. 337
4) Miyazu, T., Okuyama, Y., Fukuyama, T., Suzuki, N. and Mori, T.: Preprint for IISC, Duesseldolf, 1974, (1974)
5) Nakanura K., Hojo N. and Mori, M.: Proc. of the 44th Ironmaking Conference, Detroit, April, 1985, (1985), p. 347
6) Vorres, S.: User's Hndbook for Argonne Premium Coal Sample Program, (1989)
7) Iyama, S., Yokono T. and Sanada, Y.: Carbon, **24** (1986), p. 423
8) Yokono, T., Uno., Obara T. and Sanada, Y.: Trans. ISIJ, **26** (1986), P. 512
9) Sasaki, M. and Sanada, Y.: J. Jpn. Petroleum Inst., **34** (1991), p. 218
10) Yokono, T., Takahashi, N. and Sanada, Y.: Energy & Fueles, **1** (1987), p. 227
11) Yokono, T., Takahashi, N. and Sanada, Y.: ibid, **1** (1987), p. 360
12) Nakamura, N., Yokono, T. and Sanada, y.: Fuel Science and Technology Int'l., 8 (1990), p. 453