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Utilization of Petroleum Coke in Metallurgical Coke Making

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In Japan, NKK was the first company to use petroleum coke as the source for metallurgical coke making in 1967. Since then, petroleum coke has been utilized to increase carbon content and decrease ash content of coal blends used by Japanese iron and steel companies. This report includes the following subjects:

1. The development of the procedure for the use of petroleum coke by Japanese iron and steel companies.
2. The discussions about the effect of petroleum coke on coke strength.
3. The pitch addition as the advanced utilization.

In order to maintain high productivity in a blast furnace, it is necessary to use high-quality coke having high strength and containing few impurities such as ash and sulfur. Strength is particularly important among the properties of coke. Since coke strength largely depends upon coalification rank and fluidity of coal blends, it is possible to manufacture high-strength coke by keeping these properties at appropriate levels.

Japan imports coking coals from the United States, Canada, Australia and many other foreign countries. Future supplies of coking coals involves some uncertainty relative to procurement of good-quality coals in sufficient quantities. Various measures have been examined to solve this problem in Japan. One such measure is the expansion of the scope of raw materials used for coke-making. Use of petroleum coke as a raw material for coke-making falls into this category. Figure 1 shows annual consumptions of petroleum coke and raw materials for coke-making by the Japanese coking industry.

With a view toward the effective utilization of carbon sources, Nippon Kokan K.K. successfully utilized petroleum coke for the first time in Japan in 1967, taking advantage of the lower ash content relative to that in coals. Now that petroleum coke is used for coke-making in the Japanese coke industry as shown in Figure 1, its application may be considered as an established technology. The ratio of its use relative to coking coals is, however, still at the very low level of 1.0%. Table I shows results of examinations

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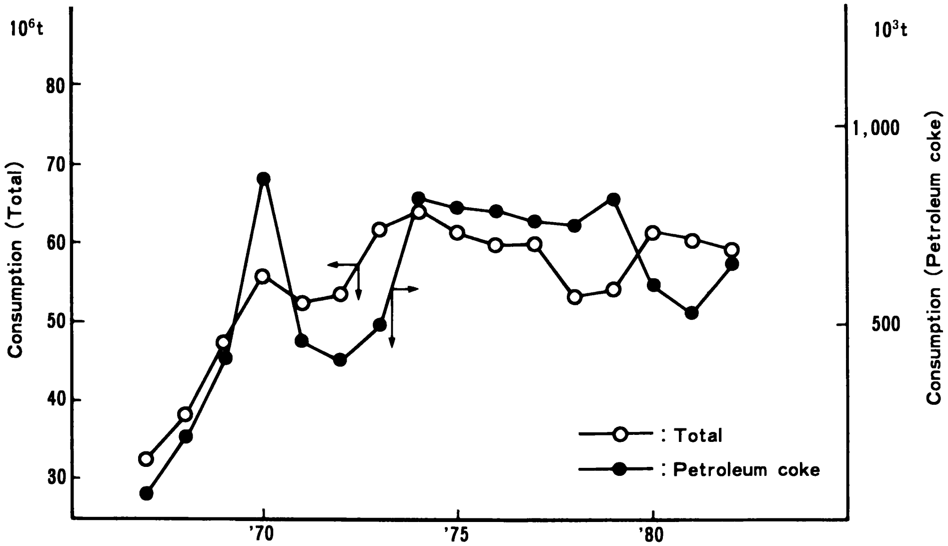


Figure 1. Annual consumption of raw materials for coke making in Japan.

Table I. Views of Japanese steel companies on use of petroleum coke

	Status of petroleum coke blending test	View on blending limit
Company A	Blending ratio: DPC: 0, 3, 5 and 7% FPC: 2, 4, 6 and 8%	1. Blending limit: 5-6%; 2. No marked difference between DPC and FPC, DPC being slightly better. 3. Increased blending of PC decreased coke ash and increased TS, and particularly because of S problem, actual use of PC is limited to about 3%.
Company B	Blending ratio: DPC: 2 and 5% FPC: 5% selective blending to partial briquetting of coal charge is also applied.	1. Blending limit is 3-5%; partial briquetting of coal charge; 2. DPC is superior to FPC.
Company C	Blending ratio: DPC: 0-15%	1. Increasing the amount of added DPC leads to almost linear decrease in DI. 2. Decrease in DI is eliminated by keeping constant $\bar{R}o$ and T.In. and maintaining MF at a certain level.
Company D	Blending ratio: DPC: 0, 5, 10 and 15% FPC: 0, 5, 10 and 15%	1. Blending limit is about 10%; 2. No marked difference between FPC and DPC.
NKK	Blending ratio: 1) To ordinary and partial briquetting of coal charge: 6% DPC 2) To partial briquetting of coal charge: 0, 2, 4, 6, 8, 10 and 12% FPC	1. Blending limit: Ordinary coal: 4-5% partial briquetting of coal charge: 8% 2. FPC is a little inferior to DPC.

regarding use of petroleum coke at the five major steel companies in Japan.(5) According to the comprehensive summary of their views, the blending limit of petroleum coke in ordinary blend relative to coking coals is about 5% at the highest, and the quality of delayed coke is better than that of fluid coke.

In this report, the authors evaluate petroleum coke as a raw material for coke-making and examine the above-mentioned blending limit. Besides petroleum coke, examination and evaluation of petroleum residual oil are also presented as a more effective use as a raw material.

Evaluation of Coking Coals

Japan imports coking coals for blast furnaces from many foreign countries. The quality of coke derived from these coals, being subject to operating conditions of the coke oven battery, mainly depends upon properties of the coking coals; coke of an excellent quality is available from appropriate combinations of coals. Blending design of coals forms one of the most remarkable features of the Japanese coke-making technology.

Blending design of coals may be summarized as follows.(1) The most important coke property is the strength, which is commonly expressed by JIS drum index in Japan. Large-capacity blast furnace engineers in Japan assert that coke should have a JIS drum strength, as expressed in DI30/15, of at least 92. Evaluation of a coking coal relative to the coke strength may be expressed with two parameters: the mean maximum reflectance of vitrinite part of coal ($\bar{R}o$) representing the degree of coalification rank of the coal, and the maximum fluidity (MF) indicating the coking property of the coal.

Figure 2 illustrates the relationship between the coke strength (DI30/15) and the maximum fluidity (MF) of blended coals in the coke oven battery at Nippon Kokan's Fukuyama Works with the reflectance ($\bar{R}o$) of blended coals as the parameter.

According to this figure, at an MF over 200 DDPM (Dial Division per Minute) with a constant $\bar{R}o$, the value of DI30/15 is maximized. Within the range of over 200 DDPM, it is necessary to increase $\bar{R}o$ which corresponds to the coalification rank of blended coals, in order to raise the strength. This range is therefore referred to as the coal rank control region. In the region of MF under 200 DDPM, it suffices to increase the fluidity (MF) of blended coals in order to raise the coke strength: this range is therefore called the fluidity control region. With an $\bar{R}o$ of blended coals of 1.15, a DI30/15 of 92 can be ensured by holding MF at 200 DDPM.

A similar test was carried out in a 20-kg test oven at Nippon Kokan's Technical Research Center as shown in Figure 3.(2) Coking conditions included a coking temperature of 880°C and a coking time of 6.5 Hrs. In this case, the coking speed is very high, so that MF corresponding to the saturation of strength is rather low at about 80 DDPM. If $\bar{R}o$ of blended coals is kept at 1.15 under these conditions, a DI30/15 of 92 can be ensured.

Use of this small-capacity test oven can facilitate an experiment, and the experiments presented in this report were conducted in this oven. In this test oven, the value of MF of 80 DDPM forms the boundary between the fluidity control region and the coal rank control region.

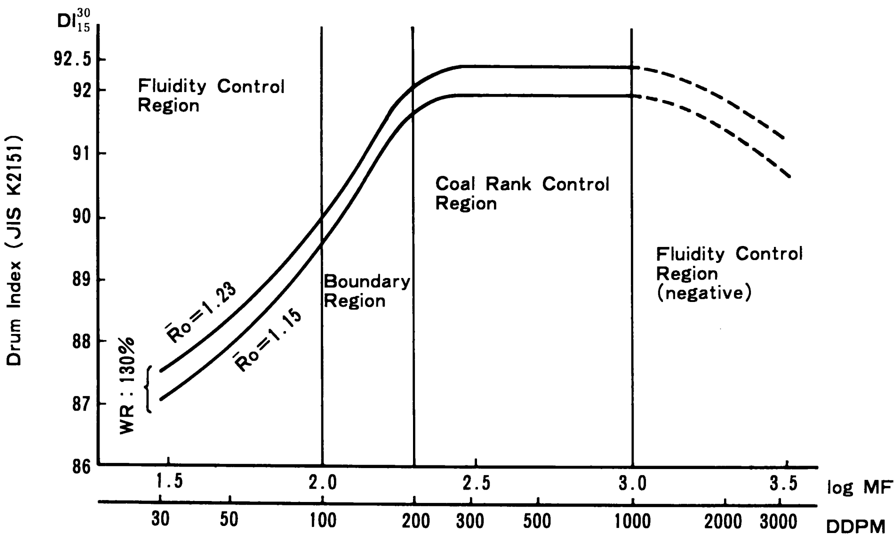


Figure 2. Relation between Gieseler max. fluidity of blends and drum strength of coke yielded in Fukuyama Works.

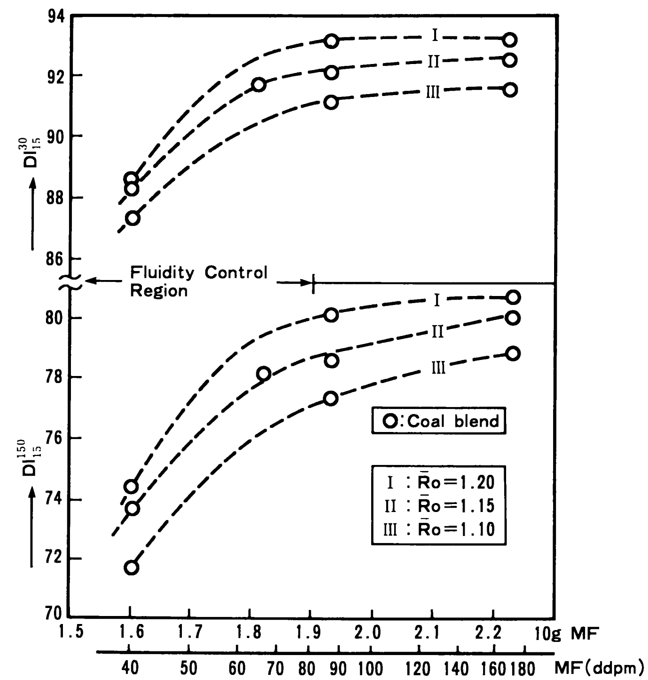


Figure 3. Relation between MF of coal blends and strength of coke made by small test oven.

Coals produced in various parts of the world may be arranged in terms of $\bar{R}o$ and MF as shown in Figure 4, which is referred to as the MOF diagram. Thus, $\bar{R}o$ and MF have significant meanings in the evaluation of a coal in terms of coke strength.

In addition to $\bar{R}o$ and MF, inert matters of coal such as ash and sulfur, which do not soften and melt, are important properties of coal to be evaluated. The relations between FOB prices of coals from various parts of the world and the above-mentioned factors were analyzed by multiple regression analysis.(3) This permits economic evaluation of coals as raw materials for coke-making. Petroleum residual oils and petroleum coke can similarly be evaluated as raw materials. The most difficult problem here is how to evaluate factors corresponding to $\bar{R}o$ and MF in coals.(6) This report presents primarily an estimation of such factors for evaluation.

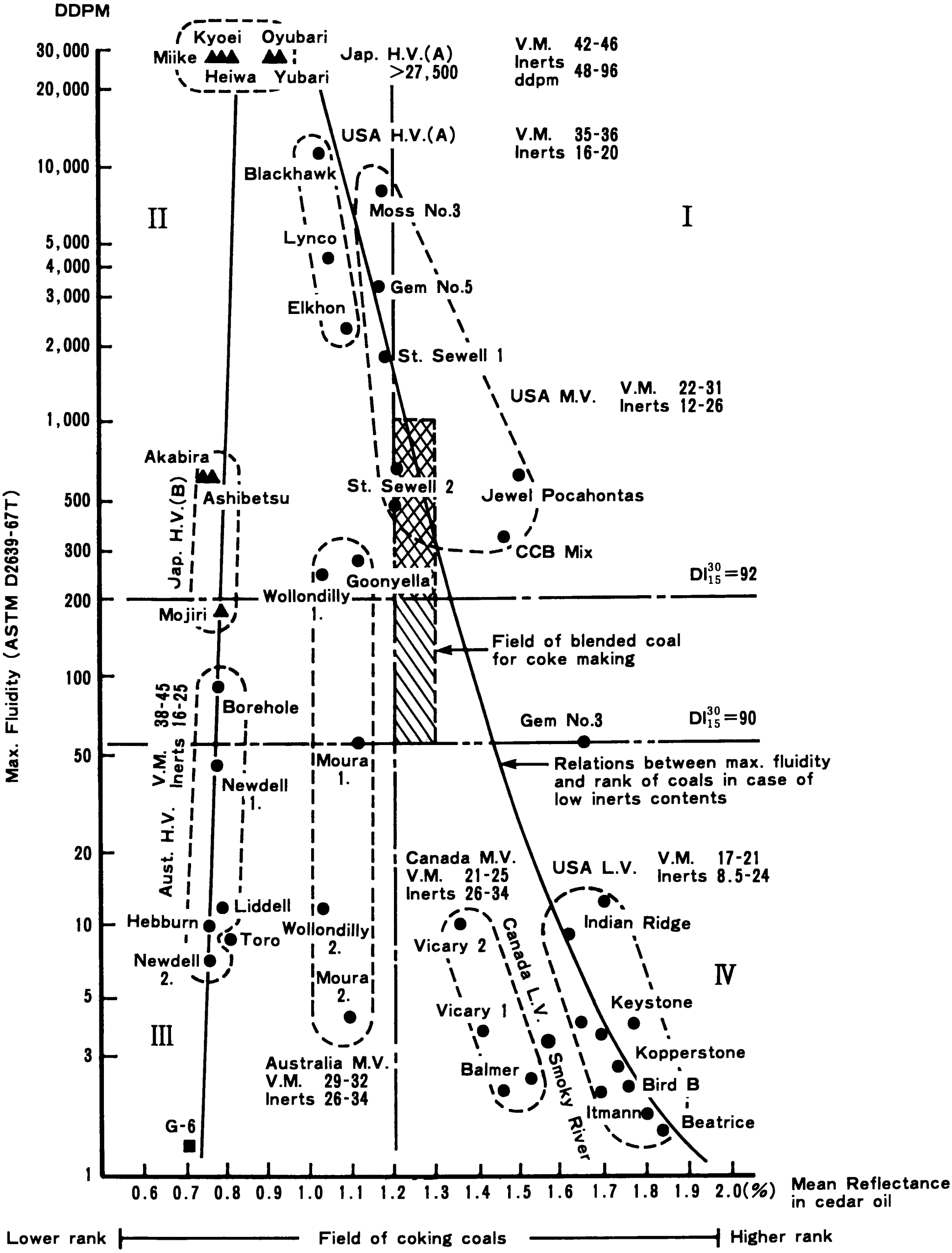
Test Method

Test Samples. Main properties of the residual oils used in the present test are represented in Table II. It should be noted in this table that: No. 1 is propane deasphalted asphalt; Nos. 2 to 7 are petroleum pitches derived from residual oil heat treated under various conditions; No. 8 is KRP pitch made by Kureha Chemical Industry from crude oil heat treated with hot steam at temperatures over 1,000°C; and Nos. 9 and 10 are both residual oils from coal, No. 9 being solvent refined coal made by NKK and No. 10 being heat treated coal tar pitch. These Nos. 1 to 10 are typical examples of binding material for coke-making in Japan.

Table II Properties of residual oil

Residual Oil (NO.)	Ash (d.b%)	VM (d.b%)	T.S (d.b%)	C/H (atomic)	Reflectance $\bar{R}o$ (%)	Reflectance $\bar{R}a$ (%)	fa	QS (%)	log (MFc)
1	tr	94.8	0.19	0.56	–	4.26	0.142	100	8.1
2	0.05	85.9	5.30	0.67	–	5.27	0.316	100	15.0
3	tr	75.7	6.75	0.82	0.30	6.25	0.471	100	13.4
4	0.80	55.5	3.75	1.03	0.43	7.30	0.581	80.2	11.1
5	0.96	40.3	6.80	1.23	1.10	9.28	0.637	85.1	11.4
6	0.38	35.1	6.44	1.29	1.05	9.11	0.651	63.7	9.2
7	0.11	36.5	5.93	1.83	0.73	7.95	0.874	83.9	14.2
8	tr	33.0	0.22	1.68	1.87	9.91	0.912	74.9	8.7
9	0.81	60.5	0.76	1.23	0.86	8.78	0.777	99.0	15.9
10	0.50	53.7	0.47	1.78	1.51	9.95	0.939	91.2	13.8

Properties of the petroleum cokes used in the present test are shown in Table III. The symbol MPC represents petroleum coke manufactured with the use of Minas heavy oil by the delayed coking process, and DPC and FPC are, respectively, petroleum cokes provided by a delayed coker and a fluid coker commercially available in Japan.



Note: V.M. contents are shown as percent on dry, ash free basis; Inerts contents are shown as volume percent.

Figure 4. Relation between max. fluidity and rank of coals (MOF diagram).

Table III. Properties of petroleum cokes

Sample	Proximate analysis (d.b.%)			Ultimate analysis (d.a.f.%)					C/H	(d.b.%)	Petrographic analysis			Calorific value (kcal/kg)
	Ash	VM	FC	C	H	N	S	O		TS	(%) Ro	(%) Ra	(vol%) Anis.	
MPC	tr	12.47	87.53	93.22	4.33	1.60	0.30	0.49	1.807	0.36	4.67	14.29	100	8,830
DPC	0.35	8.49	91.16	91.62	3.84	2.33	1.74	0.47	2.003	1.73	5.02	14.72	100	8,630
FPC	0.53	6.98	92.49	91.38	1.73	2.62	1.98	2.29	4.433	1.98	7.87	15.68	100	8,220

Residual Oil Addition Test. As previously shown in Figures 2 and 3, the effect of the reflectance and the fluidity of blended coals on the strength of coke that is produced can be expressed in the form of a model as in Figure 5.(3) Using the test oven, the low-volatile coal in the base blends was replaced by the other coals with different coal ranks in the coal rank control region, and the relationship between DI of the coke produced and $\bar{R}o$ of the replacement coal was determined. The regression line is illustrated in Figure 6.

Then, DI of the coke produced by adding residual oil in an amount equal to that of the replacement coal in the manner described above was determined, and the reflectance of the residual oil was determined from the regression line given in Figure 6. The reflectance thus determined is herein defined as the effective reflectance, $\bar{R}o_E$. After determination of $\bar{R}o_E$, DI is determined on the coke produced from a blend of coal and residual coil in the fluidity control region.

Since the values of $\bar{R}o$ of the blended coals are known, it is possible to determine the value of MF for the blend of residual oil and coals from Figure 5, and hence to determine the value of MF for the residual oil because MF for the remaining portion is known. The value of MF of the residual oil thus obtained is defined as the effective fluidity, MF_E.

Petroleum Coke Addition Test. Petroleum coke may be considered as the residual oil which is further coked. Base blends used in this addition test and the blends subjected to the addition test are shown in Table IV, which also gives the properties of the coke carbonized after blending.

When blending petroleum coke, the strength of the coke carbonized after blending is not satisfactory unless the properties of blending coals are good. The degree of contribution of petroleum coke to the coke strength is considered to be much lower than that of residual oil. This means that petroleum coke is considered to exhibit properties considerably different from those of a coking coal. With this fact in view, petroleum coke was blended on the assumption that petroleum coke was the same as the inert matter of coal, and the reactive portion was null, and takes only the fluidity into account. Examination was based on the following combinations with the base blends:

1. Changes in the strength of the coke product were studied by blending petroleum coke simply at 5% and 10% into base blends;
2. Petroleum coke is assumed to be the same as inert matter of coal as described above. Decrease in $\bar{R}o$ of the blend is compensated by coals other than petroleum coke. By considering the amount of blended petroleum coke, the blend is designed so that MF of the blend may be maintained only with that of coals in the base blend, on the assumption, however, that petroleum coke has a log[MF] of 0. Particulars in this case are shown in Table IV.

Results

Results of Residual Oil Test. Values of $\bar{R}o_E$ and MF_E as derived from the results of the test are given in Table V, which suggests that all the residual oils demonstrate excellent properties in many cases. These values are arranged into an MOF diagram in Figure 7.

Table IV. Results of petroleum coke addition test

Blended with	Properties			Blending ratio (%)												
	Ro (%)	MF DDPM	T.In. (%)	II-3	MPC	DPC	FPC	MPC	DPC	FPC	MPC	DPC	FPC		DPC	FPC
Prime (US Lv)	1.60	2	13.8	10							9.0	→	→	8.5	→	→
Pittson (US Mv)	1.10	14,000	18.1	5							4.5	→	→	4.2	→	→
Balmer (Ca.Lv)	1.36	10	34.5	30							31.5	→	→	29.8	→	→
Fording(Ca.Lv)	1.30	155	35.1	10	95	→	→	90	→	→	4.5	→	→	4.2	→	→
Wellondilly (Australia Mv)	1.08	1,000	39.2	10							9.0	→	→	8.5	→	→
Witbank(S.A.Hv)	0.84	39	36.4	25							10.1	→	→	6.0	→	→
Yutoku(Jp.Hv)	0.84	50,000	5.8	10							21.4	→	→	23.8	→	→
Petroleum coke		0	100		5	→	→	10	→	→	10.0	→	→	15.0	→	→
Properties of coal blend	Ro (%)			1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
	MF (DDPM)			136	107	107	107	83	83	83	107	107	107	107	107	107
Coke strength	JIS D^{30}_{15}			91.6	91.5	91.3	90.9	90.4	90.0	89.3	91.1	90.6	89.8	92.5	90.5	89.4

Table V Effective reflectance ($\bar{Ro}_E$) and effective fluidity (MF_E) of residual oil

Residual oil No.	Effective reflectance ($\bar{Ro}_E$)	Effective fluidity ($\log MF_E$)
1	0.027	2.55
2	0.208	5.04
3	0.377	5.98
4	0.926	5.01
5	1.144	5.99
6	1.055	5.25
7	1.228	5.38
8	1.605	6.20
9	0.924	5.95
10	1.545	5.82

<u>Results of Petroleum Coke Test</u>. The results of the test are given in Table IV. From the data shown, the relationship between the strength (DI) and the ratio of addition is represented in Figure 8. According to this figure, simple addition to the base blend results in a sharp decrease in DI, and even when $\bar{Ro}$ and MF are compensated, there is still a lower value of DI, suggesting that at least the log[MF] of petroleum coke is lower than 0.

Examination and Evaluation

<u>Examination on Residual Oil</u>. Values of $\bar{Ro}_E$ and MF_E for residual oil have been determined as described above. This measurement, however, requires much labor. Efforts were therefore made to establish a method for estimating $\bar{Ro}_E$ and MF_E from the various parameters of residual oil. Figure 9 shows the relationship between $\bar{Ro}_E$ and faQs(100 - VM); and Figure 10, the relationship between MF_E and faQs. All these figures demonstrate high correlations. These results were arranged and subjected to multiple regression analysis, and the results are given in Table VI. According to this table, $\bar{Ro}_E$ has the closest correlation with faQs(100 - VM), and MF_E' with faQs.

<u>Examination on Petroleum Coke</u>. Evaluation has been made by assuming that petroleum coke was a totally inert content and log[MF] of the fluidity was null, but this is not always the case as shown in the results in the former section.

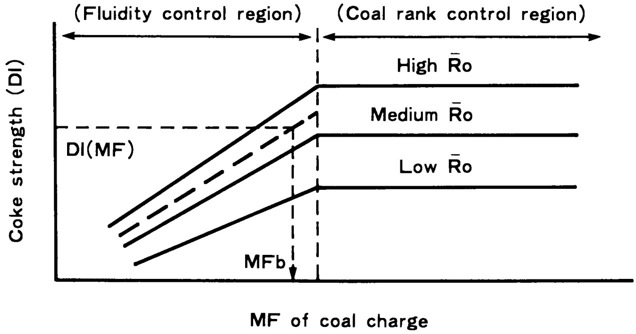


Figure 5. Effect of fluidity and coal rank of coal blend on coke strength.

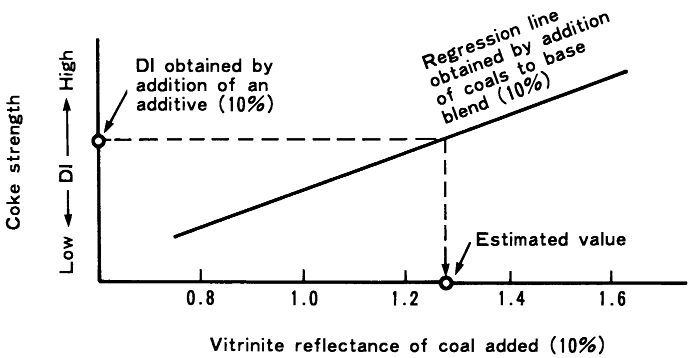


Figure 6. Estimation of effective reflectance ($\bar{R}o_E$) of caking additives.

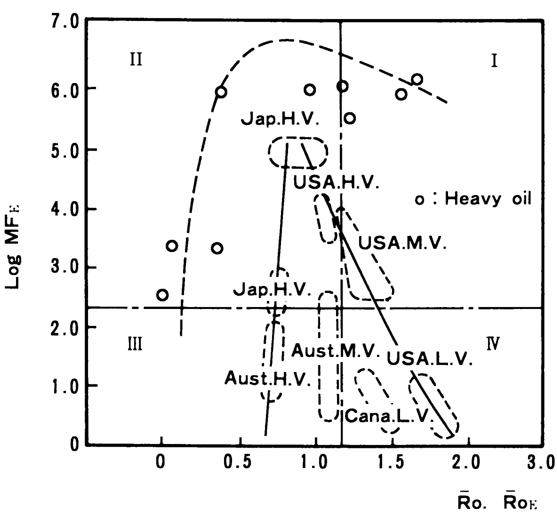


Figure 7. MOF diagram for caking additives (residual oil).

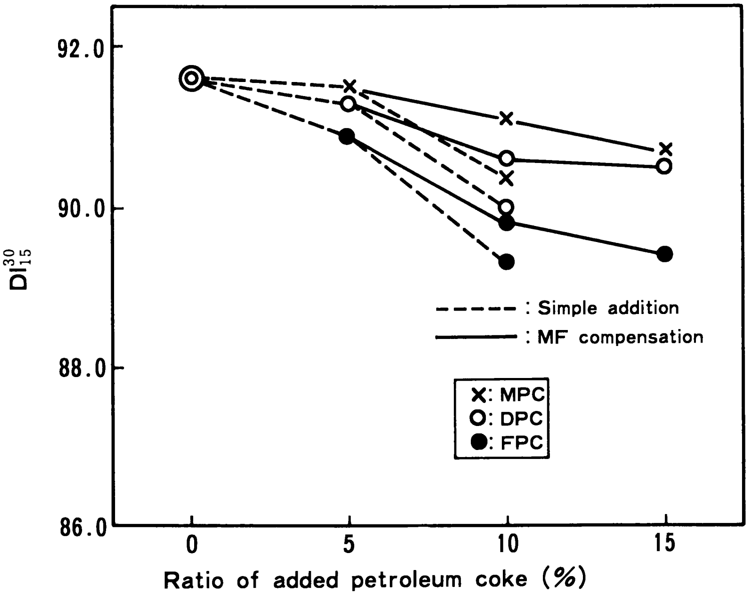


Figure 8. Change in DI30/15 by addition of petroleum coke.

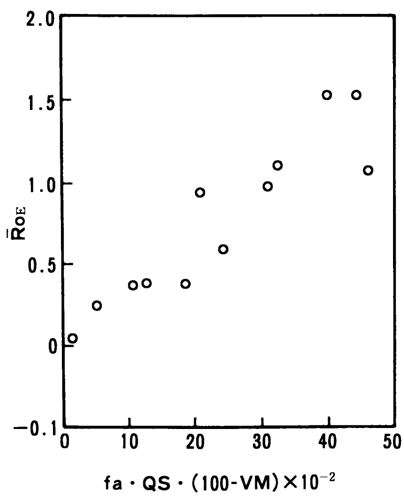


Figure 9. Relation between $\bar{R}o_E$ and faQS(100-VM).

Table VI Estimating equations of $\bar{R}o_E$ and MF_E for residual oil

$\bar{R}o_E$	$\bar{R}o_E$ = -0.02060 (VM) + 2.021 (R=-0.8167, N=56)
	$\bar{R}o_E$ = 1.1245(C/H) - 0.518 (R=0.8503, N=56)
	$\boxed{\bar{R}o_E = 0.03376(FAQS(100 - VM)) + 0.0148 \quad (R=0.9037, N=56)}$
	$\bar{R}o_E$ = 0.00285($\bar{R}$aQS(100 - VM) + 0.0287 (R=0.8724, N=52)
MF_E	$\boxed{\log MF_E = 2.445 + 5.564(FAQS) \quad (R=0.6988, N=50)}$
	log MF_E = 1.492 + 0.6024($\bar{R}$aQS) (R=0.6540, N=43)
	log MF_E = 2.429 + 0.218 log MFc (R=0.6689, N=60)
	log MF_E = 4.031 + 0.0052(TDc) (R=0.5416, N=60)

The values of MF were therefore reviewed while retaining the assumption that petroleum coke was a totally inert content. The results shown in Table VII demonstrate that log MF takes large negative values. The average of these values is defined as MF_E for a particular petroleum coke. The relationship between this MF_E and VM for petroleum coke and residual oil is represented in Figure 11, which shows the possibility of expressing MF_E by VM.

Table VII Effective fluidity (MF_E) of petroleum coke

Sample	(Simple addition) log MF_E	(MF compensation) log MF_E	(Average) log MF_E
MPC	(5%) -1.17	(10%) -2.26	-2.20
	(10%) -2.65	(15%) -2.17	
DPC	(5%) -2.75	(10%) -3.56	-3.13
	(10%) -3.70	(15%) -2.52	
FPC	(5%) -4.83	(10%) -5.66	-5.12
	(10%) -5.53	(15%) -4.44	

Note) Figures in ( ) represent blending (adding) ratios.

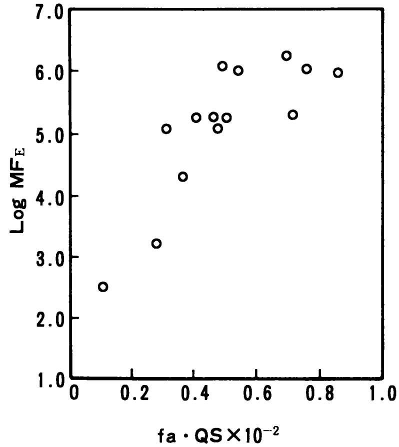


Figure 10. Relation between MF_E and faQS.

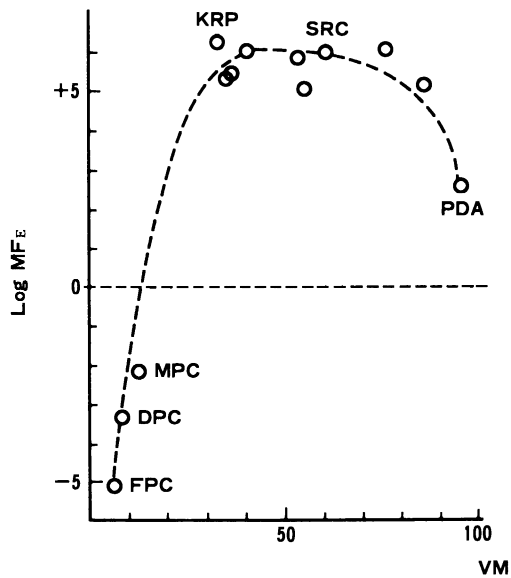


Figure 11. Relation between effective fluidity and VM of heavy residues.

Evaluation

Economic Evaluation. An additive used as a coking raw material can be evaluated from values of $\bar{R}o_E$, MF_E, inert matter, ash, sulfur and so on in the same manner as in a coal, as shown above. The relationships between the individual parameters for coal and the FOB prices have previously been determined at Nippon Kokan. These values are applicable to those of additives as shown in Figure 12.

In this figure, the price is not shown, but only the relative position was estimated by an equation. For heavy residues, the economic evaluation is shown also in this figure. In the estimation formula, C1, C2, C3 and C4 are constant coefficients determined from economic and technical points of view, and u. v. w and s are coefficients determined by multiple regression analysis.

For petroleum coke, the same evaluation is shown also in Figure 12. It will be understood that the value of petroleum heavy oil is better than that of petroleum coke as a raw material for coke making. Petroleum heavy oils can more advantageously be utilized than petroleum coke.

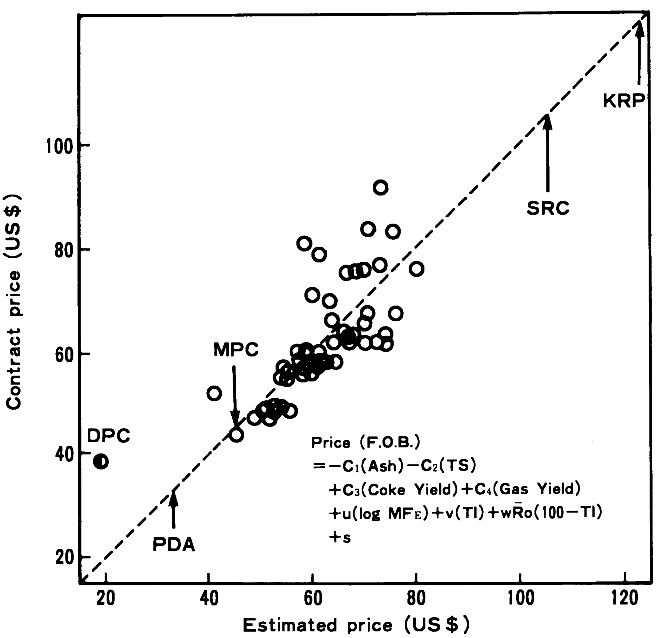


Figure 12. Relation between estimated price and contract price.

Blending Limit of Petroleum Coke. The blending limit of petroleum coke is considered to be about 5% as already mentioned above. This can be explained from the current average value of MF of about 200 to 500 DDPM for coal blends in the Japanese coking industry. Figure 13 shows limit quantities of added petroleum coke for various values of fluidity for the base coals. In the determination of these limit quantities, the quantity of added petroleum coke with which the fluidity of the coal blend decreased to below 200 DDPM under the effect of this blending was deemed as the limit.

According to Figure 13, if DPC is blended in an amount of 5% with a base blend having an MF of 400 DDPM, the resultant coal blend has a sufficient maximum fluidity (MF), whereas a 10% blending results in an MF far inferior to 200 DDPM, showing the impossibility of keeping a satisfactory coke strength. This is also the case with the other petroleum cokes, and the order is: MPC > DPC > FPC. This may be regarded as supporting the information given in Table I.

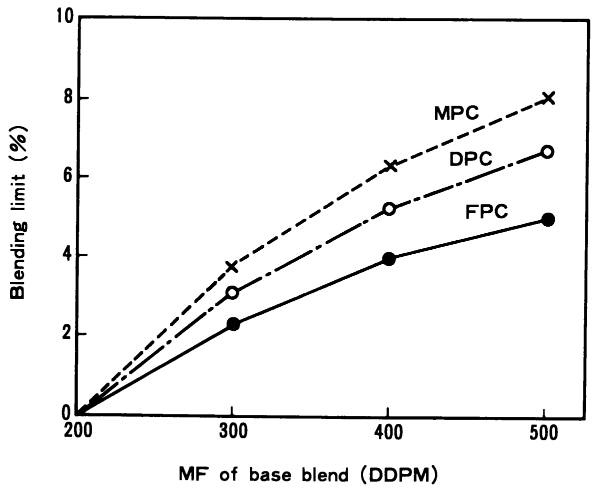


Figure 13. Blending limit of petroleum coke.

Conclusion

Petroleum coke as a coking raw material was evaluated in comparison with residual oil. While residual oil shows excellent properties as a coking raw material, petroleum coke was found to be far inferior to residual oil, and quantitative figures were determined.

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RAROP: Research Association for Residual Oil Processing in Japan

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