RESEARCH ON COAL LIQUEFACTION AND GASIFICATION

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FUNDAMENTAL STUDY ON DEVELOPMENT OF CATALYTIC COAL GASIFICATION PROCESS

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ABSTRACT

The objective of this study is to develop a catalytic coal gasification process to produce CO, H_2 and CH_4, applying the catalytic effects of mineral matters in coal if possible, and additives put artificially on coal and char. Fundamental investigations were carried out thermogravimetrically at atmospheric pressure and 700~1400°C, using various kinds of gasifying agents composed of steam(H_2O), CO_2, H_2, CO, CH_4, O_2 and N_2. An isothermal modified volume reaction(MVR) model was developed to evaluate the reactivity or rate of gasification[1].

Main conclusions were as follows:the reactivity of non-catalytic gasification of chars, prepared under similar conditions from 26 different coals of fuel ratio ranging from 1 to 20, was found to be able to correlate with two properties of the parent coals. The one was the fixed carbon content attributable to chemical structure and another was the moisture-holding capacity measured at 30°C attributable to physical structure; both could be easily analysed and determined[1,2,3,4]. The catalytic activity of mineral matter component was confirmed to be very poor for rate enhancement of gasification of carbonaceous material with steam at 800~900°C [5,6]. Then the searching for new catalysts to be added intensionally over coal/char was also confirmed to be an important research subject for the development of catalytic gasification process[5,7,8,9]. As a result, the compounds of sodium, potassium, barium and strontium were found to be very effective and promising as catalysts for gasification of char with gasifying agents consisting of steam and of CO_2, and even with the agent containing H_2S (50~500 ppm)[8,9,10,11].

NOMENCLATURE

A = preexponential factor of rate constant defined by Arrhenius equation, min^{-1}
a = constant parameter in Eq.(2)
b = constant parameter in Eq.(2)
E = activation energy of gasification of char, $kJ \cdot mol^{-1}$
f = $1-(W/W_0)$, fractional gasification of coal char, -
f_a = aromatic carbon fraction of coal, -
f_{inf} = the value of f at an inflection point on the f-θ curve, -
FC = fixed carbon content by proximate analysis of coal, wt%, db
FR = FC/VM, fuel ratio of coal, -
k = R_w/W, gasification rate based on the residual weight of combustibles in the samples, $g/g(W) \cdot min$
$\bar{k}$ = average rate constant defined by Eq.(6) according to the isothermal modified volume reaction(MVR) model, min^{-1}
R = gas constant, $kJ \cdot mol^{-1}$
R_f = $R_w/W_0 = df/d\theta$, gasification rate based on the initial weight of combustibles in sample, $g/g(W_0) \cdot min$
R_S $=R_w/S_T = k/S_f$, gasification rate based on the total surface of sample, $g/m^2 \cdot min$
R_V $=R_w/\Omega_T = k/\Omega_f$, gasification rate based on the total moisture-holding capacity given in "volume", $g/cm^3(H_2O) \cdot min$
R_w = gasification rate defined by $-dW/d\theta$, $g \cdot min^{-1}$
S_g = specific surface area of coal/char, $m^2/g(db)$
S_f $S_g[1-(1-\alpha_0)f]/[(1-\alpha_0)(1-f)]$, surface

area per weight of the combustibles in coal char, m^2/g(W)
S_T = $S_g w_0[1-(1-\alpha_0)f]$, total surface area of sample char gasified to a fractional gasification f, m^2
T = temperature, K
V_b = packing volume of coal/char bed, cm^3
V_p = Ω/ρ_{H_2O}, specific pore volume filled with moist water, cm^3(H$_2$O)/g(db)
W = residual weight of combustibles in sample coal/char, g
W_0 = initial weight of combustibles in sample coal/char, g(db)
w = residual weight of sample coal/char at f, g
w_0 = initial weight of sample coal/char, g(db)
w_s = moistened weight of coal/char at equilibrium condition, g

α_0 = fractional weight of the initial ash content in sample char. g/g(w_0)
ε_b = packing porosity of the coal/char bed, cm^3/cm^3(bed)
ε_p = $\rho_b\Omega/[\rho_{H_2O}(1-\varepsilon_b)]$, fractional of the moisture-holding volume to the apparent volume of coal/char particle, cm^3(H$_2$O)/cm^3(particle)
θ = gasification time, min
θ_{inf} = the value of θ at an inflection point on the f-θ curve, min
ρ_b = w_0/V_b, packing density of the coal/char bed, g(db)/cm^3(bed)
ρ_{H_2O} = density of the moisture(water) held in coal/char, g(H$_2$O)/cm^3(H$_2$O)
ϕ = $dT/d\theta$, heating-up speed of the temperature programed run, K/min, °C/min
Ω = $(w_s - w_0)/w_0$, moisture-holding capacity given in "weight", g(H$_2$O)/g(db)
Ω_f = $(\Omega/\rho_{H_2O})[1-(1-\alpha_0)f]/[(1-\alpha_0)(1-f)]$, moisture-holding capacity given in "volume", per the weight of combustibles in coal char, cm^3(H$_2$O)/g(W)
Ω_T = $(\Omega/\rho_{H_2O})w_0[1-(1-\alpha_0)f]$, total moisture-holding capacity given in "volume", of a sample char gasified to a fractional gasification f, cm^3(H$_2$O)

INTRODUCTION

Since the oil crisis in 1973, the development of the technology of coal as one of the alternate sources of hydrocarbon energy has been awaited eagerly all over the world. However the bars to success the development of coal gasification process are that a coal is not a pure substance but a mixture of organic matter and inorganic mineral matter, and that both of the gasification rate and the constituent of gaseous product depend strongly on the raw coal. A coal gasification proceeds in two steps: the devolatilization of coal to char which initiates near above 200°C, and then the gasification of the char with oxidizing agent such as steam, CO_2, O_2 and a mixture of these, at more higher temperature region. The former step corresponds to pyrolysis or thermal decomposition of coal with rapid rate and is referred to as carbonization in this paper hereafter. The latter is relatively slow process and can be usually regarded as a rate determination step of the coal gasification process.

It has been well known that the gasification rates/reactivities of different chars can not be independent of each parent coal, if they are prepared by the same carbonization procedure. But we have no reasonable method to predict the gasification reactivity of char with any properties of the parent coal. For our country, it is especially necessary to develop a coal gasification process applicable to any kinds of coals. So the engineering comprehension on the nature of coals, which is controlling the mechanism of gasification of coal/char, is an essential subject. This will also give an useful insight into the development of catalysts which is effective for the enhancement of rate of gasification and for the selective conversion of carbon in coal/char to CO, CH_4 or CO_2 in the produced gas. From these points of view, the experimental investigations were focussed the following subjects; (1) relation between the carbonization condition of a coal and the gasification reactivity of the char, (2) changes of the pore structure of char during gasification, (3) correlation of gasification with the chemical and physical properties of the parent coal, (4) searching and development of gasification catalysts tolerant to sulphur compounds in gasifying agent.

EXPERIMENTAL

Coal and char samples

Table 1 lists the 26 coals used and their analyses. The ultimate analyses are dry ash-free(daf) basis[2]. The proximate analyses of volatile matter(VM), fixed carbon(FC) and high-temperature ash(HTA) are dry basis, which is the weight after drying in N_2 stream at 110°C for 1 hour[1]. The coals in Table 1 have been arranged in order of their fuel ratio(FC/VM). The low-temperature ash(LTA) was the mineral matter content in the coal, as determined on an oxygen-plasma low-temperature asher(Yanaco, Model LTA-2SN). Moisture-holding capacity Ω is defined by the relative weight increase, $(w_S-w_0)/w_0$, caused by leaving the sample coal/char dried at 110°C for 25 hours into the moist air equilibrated at 30°C(or 50°C) for 60 hours[3].

The total iron content in ash in Table 1 was analyzed by a conventional chemical titration of acidic ash solution with potassium permanganese solution, and recalculated to the contents in coal and char.

A char sample was obtained by carbonizing the coal in a conventional electric furnace with various conditions at up to 1400°C, mainly for 7 minutes at 1000°C in pure N_2 stream(300 Ncm^3/min), and sieving mainly to a mean particle size of 1.0 mm(-12/+24 mesh). For convenience in this paper, the name of coal or parent coal of the char will be identified by the letters in the first column of Table 1.

Table 1 Analyses of coals

Coal		Native Country	Ultimate analysis(wt%.daf)					Proximate analysis(wt%.db)			Fuel ratio	LTA	Ω c)	Total iron content(wt%.db)		
			C	H	N	S	O_{diff} a)	Volatile matter VM	Fixed carbon FC	Ash (HTA)	$(FR=\frac{FC}{VM})$	HTA b) (—)	(10^{-2}g(H_2O)/g(db))	Coal	Char d)	Ash (HTA)
Y	Yallourn	Australia	61.2	4.8	0.5	0.1	33.5	50.7	48.6	0.7	0.96	3.70	15.4	0.15	0.31	20.8
Ta	Taiheiyo	Japan	75.8	6.5	0.9	0.2	16.7	41.9	41.6	16.6	0.99	1.52	6.5	0.52	0.89	3.1
H	Horonai	Japan	79.3	6.9	1.6	0.2	11.9	31.6	38.6	29.8	1.22	1.05	4.0	0.67	0.98	2.3
I	Illinois #6	U.S.A	79.8	5.3	1.1	2.5	11.3	37.6	50.8	11.7	1.35	1.83	7.1	0.63	1.00	5.4
M	Miike	Japan	83.9	6.5	1.2	0.6	7.8	39.0	53.7	7.3	1.38	1.41	2.4	0.41	0.67	5.6
Co	Collie	Australia	70.5	4.6	1.4	0.4	23.2	36.4	59.6	4.1	1.64	2.09	11.6	0.38	0.60	9.5
A	Abersee	Australia	79.5	5.7	2.0	0.7	12.0	33.1	56.8	10.1	1.72	1.13	3.7	0.57	0.85	5.7
L	Lithgow	Australia	82.1	5.7	1.9	0.7	9.6	31.7	57.7	10.5	1.82	1.32	4.3	0.06	0.08	0.5
W	Woodland	Australia	82.8	5.8	1.7	0.5	9.2	31.3	57.9	10.8	1.85	1.04	5.7	0.64	0.93	5.9
KM	Kellerman	U.S.A	82.6	5.9	1.8	0.5	9.2	34.5	64.5	1.0	1.87	1.65	3.6	0.09	0.14	9.2
Za	Zaozhong	P.R.China	83.7	5.1	1.3	0.3	9.5	31.7	61.4	6.9	1.94	1.59	2.3	0.16	0.24	2.4
Ma	Matla	R.S.Africa	77.7	5.9	1.9	0.6	13.8	31.2	61.7	7.1	1.98	1.32	8.6	0.11	0.16	1.5
Z	Zontagsvlei	R.S.Africa	83.9	5.8	2.1	0.6	7.7	30.2	63.4	6.4	2.10	1.45	6.1	0.83	1.19	13.0
BA	Blair Athol	Australia	78.6	5.3	1.6	0.5	14.0	27.2	62.7	10.2	2.30	1.07	8.5	0.14	0.20	1.4
BW	Black Water	Australia	79.4	5.1	2.0	0.4	13.2	27.0	65.6	7.4	2.43	1.49	3.5	0.60	0.83	8.1
Ca	Callide	Australia	75.6	4.8	1.1	0.2	18.3	26.7	65.9	7.4	2.47	1.85	9.4	0.22	0.30	3.0
D	Datung	P.R.China	85.4	5.2	0.9	0.4	8.1	25.9	64.8	9.3	2.50	1.18	4.8	0.17	0.23	1.8
K	Kailuan	P.R.China	88.3	5.2	1.2	0.6	4.8	21.1	65.0	13.0	3.08	1.21	1.4	0.24	0.30	1.8
B	Balmer	Canada	83.7	4.6	1.2	0.4	10.2	22.1	69.1	8.8	3.13	1.29	1.8	0.16	0.20	1.8
P	Pittstone	U.S.A	85.6	4.1	1.3	0.7	8.3	19.3	77.4	3.3	4.00	1.32	1.7	0.42	0.52	12.8
S	Smoky River	Canada	86.4	4.5	1.2	0.6	7.4	17.8	75.1	7.1	4.21	1.67	1.8	0.25	0.30	3.5
Ky	Keystone	U.S.A	91.2	4.8	1.3	1.0	1.7	15.4	79.0	5.6	5.12	1.62	2.2	0.33	0.38	5.8
Ku	Kuznetsk	U.S.S.R	88.1	4.3	1.7	0.7	5.2	13.0	79.0	8.1	6.10	1.18	2.4	0.18	0.21	2.2
U	Uonuki	Japan	89.6	4.5	1.7	0.9	3.3	10.1	80.1	9.8	7.91	1.21	3.9	0.56	0.62	5.7
PB	P. R. O. C. B	P.R.China	89.7	4.0	1.0	0.9	4.4	7.5	76.1	16.4	10.10	1.45	3.5	0.43	0.47	2.6
V	Hon-Gai	Vietnam	93.4	3.5	0.9	0.3	1.9	4.5	89.7	5.9	20.04	1.78	3.8	0.12	0.12	2.0

a) O_{diff} = 100-(C+H+N+S)
b) LTA : Mineral matters in coal derived by the oxygen plasma asher at low temperature
c) Moisture-holding capacity of coal, defined to be the equilibrium moisture content at 30°C
d) Char was prepared by thermal decomposition of coal in nitrogen stream for 7 min. at 1000°C

As a model for the cabonaceous material of coal/char containing no inorganics, the porous pure carbon(PPC in short) was prepared by the programed thermal decomposition of copolymer resin powder of PVDC(70%) and PVC(30%), from room temperature to 900°C at a heating-up speed of ϕ = 4°C/min in N_2 stream, and PPC was used for a reference comparable with coal/char[5,7,8].

Apparatus and procedure[1,2,5]

The gasification runs were carried out by three experimental systems shown in Fig. 1. The system is the combination of a thermobalance with two sets of gaschromatographs, and makes it possible to monitor the rate of gasification and the gaseous products(H_2, CO and CO_2) at exit of the reactor simultaneously. The NO content of the exit gas was also monitored continuously on a chemical-luminescence-mode NO_x meter (Yanaco, model ECL-77) for the gasification with oxygen. Three different types of thermobalances were used in each system: Type I(Shimadzu, model TM-2) = manual recording mode, installed a quartz reaction tube of internal diameter(I.D.) 29 mm and a conventional radiation furnace used for low temperature run below 1000°C with gasifying agent containing even H_2S and COS, Type II (Shimadzu, model DT-30) = auto recording mode, installed an alumina reaction tube of I.D. 16.5 mm and a platinum-heater furnace used for high temperature run up to 1400°C, Type III(Shimadzu, model DT-30) = auto recording mode, installed a quartz reaction tube of I.D. 16.5 mm and an infrared-ray furnace capable of rapid heating and quenching of the sample solid.

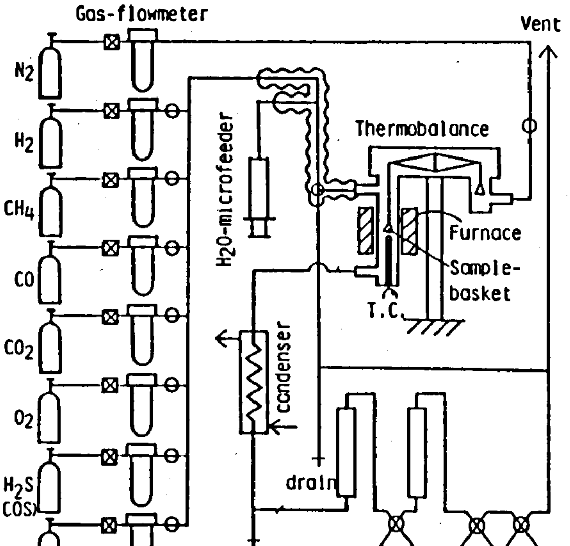

Fig.1 Schematic diagram of the apparatus for gasifications of coal and char

The gasifying agent used for gasification runs were mixture of $H_2O(0\sim41\%$, mainly 24%), $CO_2(0\sim60\%)$, $H_2(0\sim30\%)$, $CO(0\sim15\%)$, $CH_4(0\sim6\%)$, $O_2(0\sim21\%)$, H_2S,COS,NO,HCN,NH_3(0 $\sim$ 500 ppm) and N_2 for balance. The total flow rates of the gasifying agent were 500 Ncm^3/min with Type I apparatus and 400 Ncm^3/min with the Type II and Type III apparatuses. In the experiments at below 1050°C, the sample coal/char(150, 200 mg) was packed into a basket made of thin quartz rod and covered with a thin layer of fine quartz wool. In the catalytic experiments(150 mg) and the noncatalytic experiments at high temperature of 1100$\sim$1400°C(30 mg), sample char was packed into a platinum-gauze basket(80 mesh). The sizes of the two baskets were internal diameter(I.D.) 20 mm X height 10 mm for the Type I and I.D. 13.5 mm X height 7 mm for the Types II and III. In each case, the samples coal/char particles were packed as loosely as possible. It had been ascertained that the effects of the flow rate of gasifying agent and the sample weight to be loaded were negligible at these experimental levels.

The specific surface areas of the representative char samples, and of the chars during the course of the gasification, were determined from the N_2 adsorption at 78 K(Sg(N_2)) and the CO_2 adsorption at 187 K(Sg(CO_2)) as measured on a gaschromatographic apparatus(Shimadzu,model ADS-1B) using the Langmuir equation.

X-ray diffraction analyses were conducted over coal, char, LTA and ash(HTA), to identify mineral matters in coal and to determine any crystalline changes of mineral matters and additives upon gasification.

KINETIC MODEL[1 8]

The fractional gasification of char f is defined as the weight loss$(W_0 - W)$ standardized on W_0. The experimental data from isothermal gasification run is primarily shown as a curve of fractional gasification f versus gasification time θ. Different definitions, such as R_W, R_f and k, are possible for the gasification rate at any points on the f-θ curve, e.g.,

$$k = -(dW/d\theta)/W = (df/d\theta)/(1-f) \tag{1}$$

The following procedures were applied to analyze the experimental f-θ data and to evaluate quantitatively the gasification reactivity of the char:

(i) Experimental f-θ data were substituted into the linearized form of the modified volume reaction(MVR) model Eq.(2), and the values of the parameters a and b were determined by the least-squares method.

$$f = 1 - \exp(-a\theta^b) \tag{2}$$

$$\left.\begin{aligned} &Y = \ln(a) + bX \\ &\quad Y = \ln[-\ln(1-f)],\ X = \ln(\theta) \end{aligned}\right\} \quad (3)$$

A simple analysis of Eq.(2) reveals that, when $0 < b \leqq 1$, there is no sigmoidal(S-shaped) character on the f-θ curve, the gasification rate R_f decreasing with time. When b = 1, Eq.(2) is identical with the equation for chemical-reaction rate control in the continuous model[12]., with the parameter "a" then being the rate constant of the first order reaction. If b > 1, a sigmoidal character occurs, and the values of θ and f corresponding to the point of maximum gasification rate on the f-θ curve are given by the equations,

$$\left.\begin{aligned} &\theta_{inf} = [(b-1)/ab]^{1/b} \\ &f_{inf} = 1-\exp[-(b-1)/b] \end{aligned}\right\} \quad (4)$$

Eq.(2) can follow any curve even whose R_f is at a maximum for any f between 0 and 1, unlike the rate equation of Bhatia et al[13].

(ii) When the values of the parameters a and b were determined, the specific rate of gasification k took the form,

$$k = a^{(1/b)}b[-\ln(1-f)]^{(b-1)/b} \tag{5}$$

Eq.(5) is available to calculate the gasification rates by other definitions such as R_f, R_s and R_V at any points on the f-θ curve.

(iii) As an index of gasification reactivity, the average rate constant $\bar{k}$ was calculated from the definition,

$$\bar{k} = \int_0^1 k\,df \doteqdot \int_{0.01}^{0.99} k\,df \tag{6}$$

The value of $\bar{k}$ is also expressible with reasonable accuracy in terms of the rate, k at f = 0.50.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Moisture-holding capacity of coal/char[3]

Almost all of the dry samples of coal and char were saturated with moisture within about 60 hours at 30°C and 50°C both (Fig.2). No differences were found in the moisture-holding capacities Ω measured at 30°C and 50°C. The packed densities of dry samples, ρ_b ranged narrowly from 0.60 to 0.75 for 26 coals, but ranged from 0.3 ~ 0.9 for the chars carbonized in N_2 stream for 7 min at 1000°C. However also no significant differences were found in $\Omega\,[g(H_2O)/g(db)]$ (Fig.3) and $\rho_b\Omega\,[g(H_2O)/cm^3(bed)]$, between the coals and their chars. The moisture held in coal/char is reasonably assumed to fill the micro pore which predominates over the total pore volume(Fig.4)[14]. Since Ω is proportional to the specific pore volume, $V_p(=\Omega/\rho_{H_2O})$

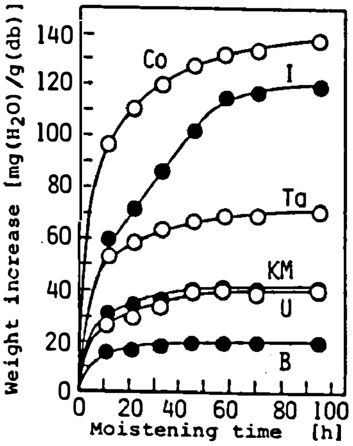

Fig.2 Weight increases of the dry coals by moistening at 50°C

to be filled with moist water, and $\rho_b\Omega$ is also proportional to the porosity of sample ε_p, the findings stated above suggest the micro pore structure will not be altered drastically by carbonization process of coal to the char. This will be one of the support for the conclusion that the gasification reactivities of chars can be correlated with properties of the parent coals.

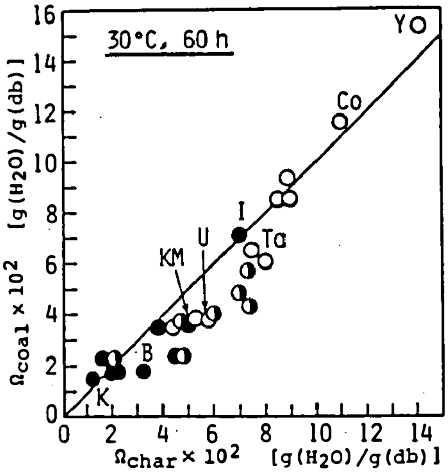

Fig.3 Moisture-holding capacities of coals and their chars carbonized in N_2 stream for 7 min at 1000°C

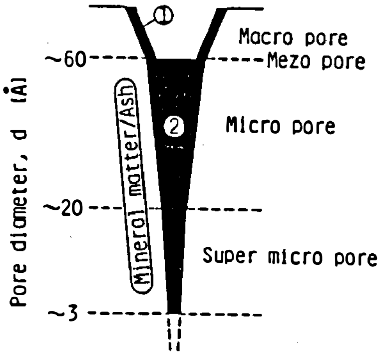

Fig.4 Model on the moisture held in the pore of coal/char
① The adsorbed phase with mono/multi layer mode
② The condensed phase

History effects of the carbonizations of coal[15]

Heating-up speed in carbonization step:

The 11 coals were gasified with H_2O(24%)-N_2 mixture by temperature programed condition that raising temperature from 110°C up to 850°C at different heating-up speeds ϕ = 5~420°C/min followed holding isothermally at the ceiling temperature(T_c) of 850°C(Fig.5), described shortly as 110°C (ϕ[°C/min]) 850°C. The O-keys on the curves in Fig.5 indicate the points to be at 850°C. Since all of the fractional gasifications of the coal at the points is nearly equal to VM of the coal, the part of the curve operated isothermally at 850°C can be regarded as the gasification of the char prepared with different heating-up speeds(ϕ). The reactivity of the char was

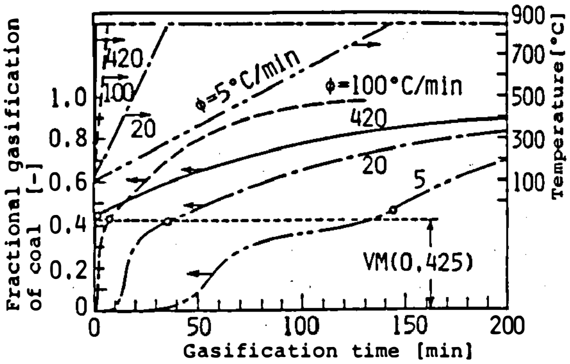

Fig.5 Temperature programed gasifications of Illinois#6 coal with H_2O(24%)-N_2 mixture at heating-up speeds ϕ=5~420°C/min from 110°C to 850°C

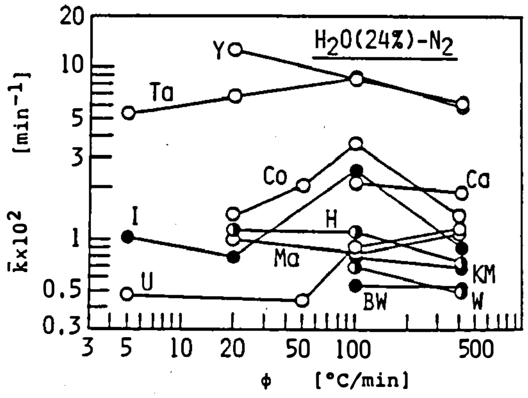

Fig.6 The heating-up speed(ϕ) during carbonization of coal and the average rate constant($\bar{k}$) for the isothermal gasification of the char at 850°C

analyzed by MVR model Eq.(2), and in Fig.6, $\bar{k}$ was composed with ϕ. But any constant trend was not found between them, and the ratio of the maximum $\bar{k}$ to the minimum was within only about 3 at most for any coals.

Carbonizations at 200°C~800°C(Incomplete devolatilization):

Three coals were carbonized to the chars in N_2 stream by temperature programed mode of 110°C(10°C/min) T_c, and succeedingly the chars were gasified with H_2O(24%)-N_2 mixture at 880°C isothermally, and their reactivities were evaluated with $\bar{k}$(Fig.7). T_c was set at 200, 300, 400, 600 and 800°C, but the devolatilization of coal was not completed in these carbonization levels

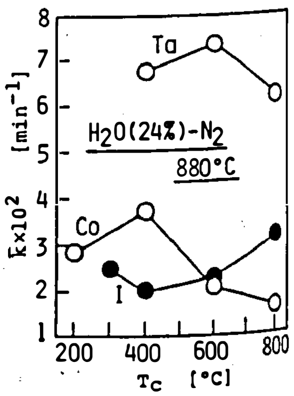

Fig.7 The ceiling temperature(T_c) in temperature programed carbonization of coal,110°C(10°C/min) T_c,in N_2 stream and the reactivity of the char for H_2O-gasification at 880°C

except for the run at T_c = 800°C. The effect of T_c in carbonization, assessed with the ratio of the maximum $\bar{k}$ to the minimum, did not exceed 2.3 for any coals in this study.

Carbonizations at 900°C~1400°C:

The 6 kinds of coals were carbonized in N_2 stream for 7min at a relatively high temperature ranging 900°C to 1400°C. The yield and the specific surface area of the char were almost independent of the carbonization temperature. However, as shown in Fig.8, significant differences were detected in the reactivities of the chars for the H_2O gasification at 900°C. When the carbonization temperature was raised up from 900°C to 1300°c, Collie char did not show so distinct changes in reactivity, but Blackwater char and Uonuki char lost their reactivities to be 1/7 and 1/10, respectively. These changes in reactivity could be explained well with the moisture-holding capacity(Ω) of the char[3].

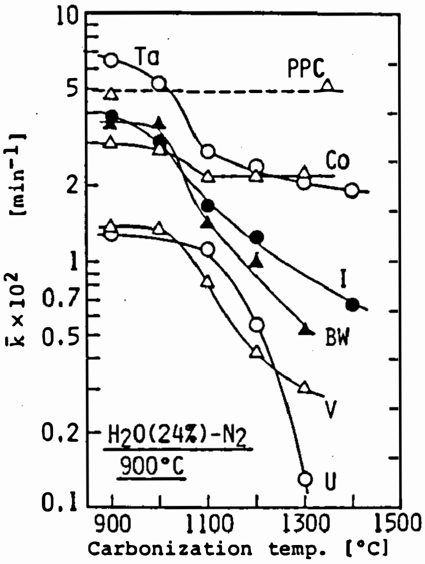

Fig.8 Effect of carbonization temperature of coal on the gasification reactivity($\bar{k}$) of the char

Changes of pore structure during gasification[3]

Fig.9 shows typical examples of the fitting of MVR model Eq.(2) to the experimental data(○ , ●) of H_2O-gasifications of three kinds of chars different in ash content α_0. Sg(N_2), Sg(CO2) and $\Omega_{30°C}$ were measured for the sample chars equivalent to ●-keys shown in Fig.9, and other physical parameters attributable to pore structure of char, such as $S_T(N_2)$, $S_T(CO_2)$, $S_f(N_2)$, $S_f(CO2)$, Ω_T and Ω_f, and their relations with gasification rate at each ●-point were discussed in detail. Since the gasification rates of these runs have been confirmed to be of chemical reaction controlling[2, 4], if the surface concentration of active site for gasification is kept constant, gasification rates such as R_S based of surface area and R_V based of pore volume should be also constant while gasification is on, and the reactivities of the chars should be close each other. But, this was not fully satisfied with our experimental results (Fig.10).

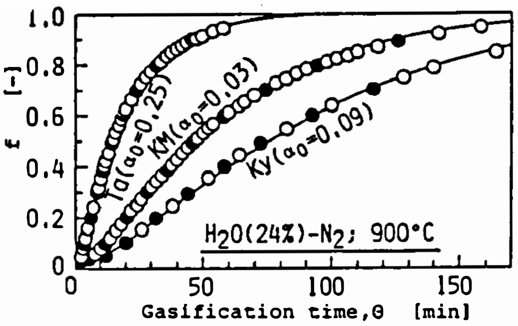

Fig.9 Fitting of MVR model Eq.(2) (——) to the gasification data of char(○,●), carbonized in N_2 stream for 7 min at 1000°C

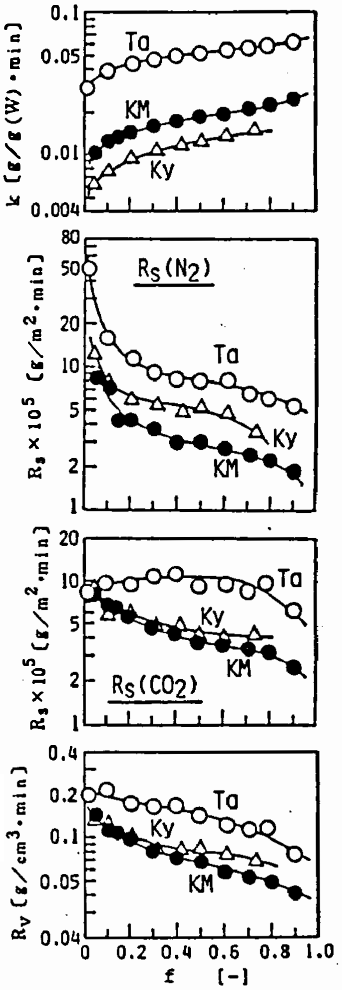

Fig.10 Changes of the gasification rates by different definitions/ methods (See Fig.9)

Gasification reactivity of char

Coal rank:

The gasification system, I~VII shown in Table 2, were tried to compare the gasification reactivities of chars. In every system, sample chars were carbonized by the same condition. In all of these cases, the reactivity of char was strongly dependent on the parent coal(Fig.11). Not only $\bar{k}$, but $\theta_{50\%}$, θ at f = 0.5 in Fig.11, was an useful measure of relative reactivity of the char, and all of the f-θ curves get by the systems I, VI and VII in Table 2 was unified to a

Table 2 Gasification systems for the evaluation of reactivity of coal char

	Gasification of char			Preparation of sample char	
	Gasifying agent	Temp. [°C]	Number of sample char	Thermal decomposition of coal in N_2 stream	Ref.
I	$H_2O(24\%)-N_2$	850	23	900°C, 60min	1
II	$H_2O(24\%)-N_2$	950	16	1000°C, 7min	6
III	$H_2O(24\%)-H_2(24\%)-N_2$	950	17	1000°C, 7min	6
IV	$H_2O(24\%)-H_2(24\%)-H_2S(200ppm)-N_2$	950	16	1000°C, 7min	6
V	$H_2O(24\%)-CO_2(24\%)-H_2(30\%)-CO(15\%)-N_2$	1000	13	1000°C, 7min	16
VI	$CO_2(20\%)-N_2$	950	23	1000°C, 7min	2
VII	$O_2(10\%)-N_2$	900	26	110°C(20°C/min)900°C(30min)	1

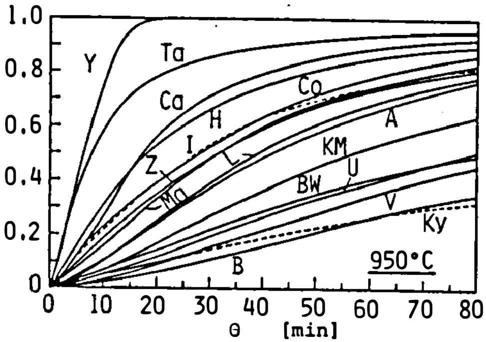

Fig.11 Gasification of chars with a mixture of $H_2O(24\%)-H_2(24\%)-H_2S(200 ppm)-N_2$ (See Fig.14)

$f-(\theta/\theta_{50\%})$ curve, respectively[1,2].

Temperature[2]:

The 4 kinds of coal chars, which were prepared in N_2 stream for 7 min at 1000°C, were gasified with mixtures of $H_2O(24\%)-N_2$ and $CO_2(20\%)-N_2$ at temperatures ranging from 800°C to 1400°C(Fig.12). Ash in some sample char was found to be melted at above 1300°C by optical observation, what was indicated with black keys in Fig.12. But the relative order of reactivity among the chars held consistently good at these temperature levels for both gasifying systems.

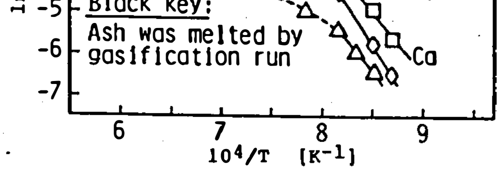

Fig.12 Arrhenius plot of k̄ in CO_2-gasification of coal chars

Gasifying agent:

Gasification rate of a char was depressed when a reductive gas component, such as H_2, CO and CH_4, was mixed with gasifying agents composed of oxidative H_2O and CO_2 [4,7,16]. The rate of gasification with $H_2O(24\%)-O_2(1\%)-N_2$ mixed with low level CH_4 (3~6%) was almost close to the rate with $O_2(1\%)-N_2$, and the product gas was rich in CO and H_2 although CH_4 was not consumed at all. This was interpreted well by the homogeneous radical chain oxidation scheme of CO and H_2[4]. The relative potentials of the three gasifying agents for gasification were compared in Fig.13[16].

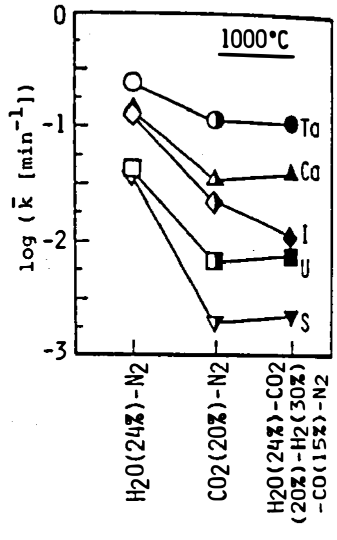

Fig.13 Effect of the gasifying agent on the gasification reactivity of char

Kinetic analysis[2]:

The kinetic analyses were carried out, in detail, in the chemical reaction controlling region below 1000°C, and the results were summarized in Table 3.

Table 3 Kinetic analyses of gasifications of coal chars with steam and CO_2[2]

	$\bar{k}=k_0\,p^m\,(d_p)^n\,\exp(-E/RT)$					
Gasifying agent	$H_2O-(N_2)$ mixture			$CO_2-(N_2)$ mixture		
Parent coal	m1)	n	E	m	n	E
Taiheiyo	0.43	0	191	0.502)	0	197
Illinois#6	0.43	0	195	0.542)	0	308
Callide	0.42	—	197	0.472)	—	257
Uonuki	0.67	—	157	0.453)	—	241

Particle pressyre: P_{H_2O}=0.16~0.41[atm], P_{CO_2}= 0.1~0.6[atm]
Particle diameter: d_p=0.5~2.0[mm]
Activation energy: E [kJ/mol]
1) 900°C, 2) 950°C, 3) 1000°C

Correlation of the reactivity of char

To explain the defference in gasification reactivity(k̄) found among the chars carbonized with the same condition, FR and H/C (atomic ratio) of their parent coals were discussed to be fairly good parameters[1,2].

Table 4 Correlation coefficients derived by the regression analyses of the gasification reactivities of chars with the various properties[1] of char and parent coal. (See Table 2)

$\log(\bar{k}\ [\mathrm{min}^{-1}]) = A_0 + A_1 \log(X_1) + A_2 \log(X_2)$												
X_1	Ω_{char}	$(\rho_b\Omega)_{char}$	Ω_{coal}	$(\rho_b\Omega)_{coal}$	$[C]_{coal}$	$[C]_{coal}$	$(H/C)_{coal}$	$(H/C)_{coal}$	$f_{a\,coal}$	$f_{a\,coal}$	FC_{coal}	FC_{coal}
X_2						Ω_{coal}		Ω_{coal}		Ω_{coal}		Ω_{coal}
I	0.706[2]	0.662[2]	0.747	0.759	0.714	0.779	0.852	0.918	0.648	0.904	0.774	0.910
II	0.784	0.513	0.782	0.731	0.858	0.876	0.789	0.928	0.671	0.936	0.818	0.955
III	0.816	0.525	0.789	0.738	0.777	0.829	0.711	0.885	0.645	0.913	0.754	0.914
IV	0.858	0.656	0.828	0.778	0.812	0.869	0.657	0.892	0.546	0.910	0.717	0.927
V	0.645	0.688	0.633	0.647	0.547	0.637	0.650	0.706	0.591	0.737	0.654	0.749
VI	0.709	0.728	0.752	0.754	0.681	0.770	0.682	0.821	0.525	0.844	0.679	0.859
VII	0.527**	0.310**	0.554	0.483	0.808	0.811	0.808	0.829	0.609	0.748	0.792	0.825

[1] Ω : Moisture-holding capacity measured at 30°C. [C] : Carbon content given in wt%,daf. (H/C) : atomic ratio. f_a : Aromatic carbon fraction. FC : Fixed carbon given in wt%,db.

[2] Approximated with values ($\Omega, \rho_b\Omega$) of char prepared by thermal decomposition in N_2 stream for 7 min at 1000°C

But the regression analyses with a form of Eq.(7) were found to give the best correlations for all of the seven gasification systems in Table 2(Table 4), and to be available to estimate the unknown rate/reactivity of a char with the chemical and physical properties of the parent coal(Fig.14)[3].

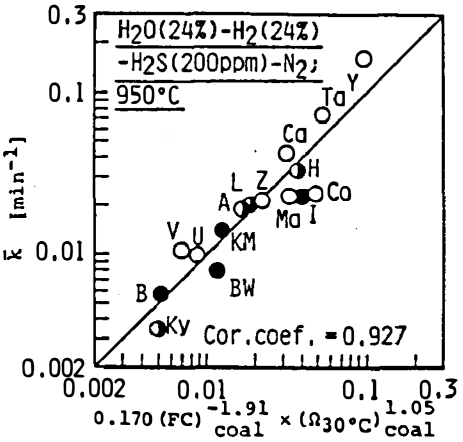

Fig.14 Regression analysis of the gasification reactivity($\bar{k}$) of char with the properties of parent coal (See Fig.11, Table 4)

$$\left.\begin{array}{l} \bar{k}_{char} = 10^{A_0}(FC_{coal})^{A_1}(\Omega_{coal})^{A_2} \\ (A_0,\ A_1,\ A_2\ :\ \text{constant}) \end{array}\right\} \quad (7)$$

Catalytic activity of mineral matter in coal[5,10,11].

From the above findings on gasification, the catalytic activities of rate enhancement and CO-shift reaction($CO + H_2O = CO_2 + H_2$) which were attributable to mineral matters in coals, seemed to be extremely poor or at close level among the coals. This points was asserted by the experiment on H_2O-gasification of the model chars prepared by loading LTAs of three coals and typical ash components, such as SiO_2, Al_2O_3, TiO_2 and Fe_2O_3 into PPC[5]. But there were some coal ash to show good catalytic activities for chemical conversions of low level NO, HCN and NH_3 contained in a gasifying agent of $H_2O-H_2-H_2S-N_2$ mixture, and iron oxide was found to be the most responsible component in ash(Table 5)[10].

Table 5 Catalytic activities of coal ash and ash components for the conversion of N-compound in a gasifying agent of $H_2O(10\%)-H_2(2.5\%)-H_2S(500ppm)-\{NO,HCN,NH_3\}(500ppm)-N_2$ mixture[1] [10]

Reaction[2]	$NO \rightarrow NH_3$	$HCN \rightarrow NH_3$	$NH_3 \rightarrow N_2$
Taiheiyo coal ash	◎	◎	×
Datung coal ash	◎	◎	○
SiO_2	×	×	×
Al_2O_3	△	△	×
CaO	◎	△	×
Fe_2O_3	◎	◎	◎

1) Temperature: 800~950°C, Space velocity = 6×10^4 [h^{-1}]

2) $NO+(5/2)H_2 \rightarrow NH_3+H_2O$, $HCN+H_2O \rightarrow NH_3+CO$, $NH_3 \rightarrow (1/2)N_2+(3/2)H_2$

Catalytic activity: ◎ good, ○ moderate, △ poor, × not identified

Catalytic additives over coal/char

Investigation were carried out on the catalytic potential and feasibility of the transition metal(Fe, Co, Ni) compounds[7], the alkaline earth metal(Mg, Ca, Sr, Ba) compounds[5,8], and the alkali metal(Li, Na, K) compounds[7,9] for H_2O- and CO_2-gasifications of PPC and coal chars. The catalytic rate enhancement were seemed to be caused by the reaction cycles; $Fe \rightleftharpoons FeO$, to produce synthesis gas($CO + H_2$)[5,7], $Ba(OH)_2 \rightleftharpoons BaCO_3$, and $BaS \rightleftharpoons BaSO_4$ for H_2O-gasification. $BaO{\cdot}BaCO_3 \rightleftharpoons BaCO_3$ for CO_2-gasification[5,8,9]. Alkali and alkaline earth compounds also promoted CO-shift reaction to produce a gas rich in H_2 and CO_2[5,7,8,9].

Sulphur tolerance of the catalyst[9]

The Fe, Ni, Ba, Na and K compounds and sea water, all the effective catalysts, were tolerant to H_2S and COS(~400 ppm) mixed with a gasifying agent of H_2O (24%)-N_2 for the gasification of PPC and chars at 800 ~ 900°C. Besides, the Ba, Na and K compounds and sea water held good catalytic rate enhancement in the gasification with H_2O (24%)-H_2(24%)-H_2S, COS(100~400 ppm)-N_2 mixture (Fig.15, Fig.16) and were very promising catalysts to be studied further. Another subject to be investigated further was the dependence of catalytic rate promotion on the coal (Fig.16) and the procedure to add the catalyst over coal and char.

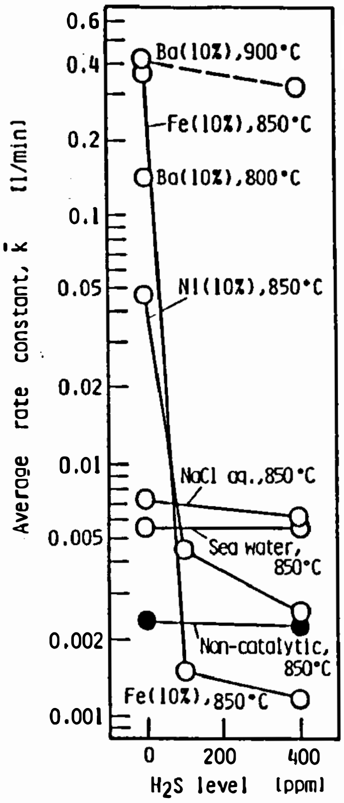

Fig.15 Effect of H_2S in gasifying agent on the rate of catalytic gasification of PPC with a mixture of H_2O(24%)-H_2(24%)-H_2S(0 ~ 400 ppm)-N_2

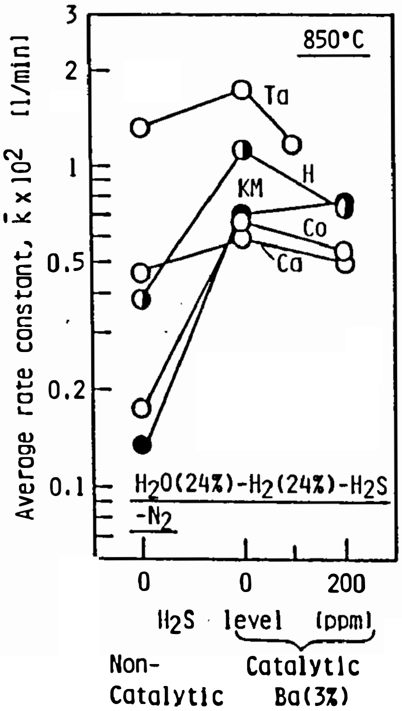

Fig.16 Catalytic rate enhancement by Ba(3%) impregnated over chars, and their tolerance to H_2S(200ppm) in a gasifying agent

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