* = normalization for dilute solution
∘ = reference state

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A NEW KINETIC MODEL FOR TEMPERATURE PROGRAMED THERMOGRAVIMETRY AND ITS APPLICATIONS TO THE GASIFICATION OF COAL CHARS WITH STEAM AND CARBON DIOXIDE

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For the kinetic analysis of non-catalytic solid-gas reaction by thermogravimetry, the rate equation $f = 1 - \exp[-a(T-c)^b]$, (f = fractional conversion of reactive solid, T = temperature, a, b, c = constants) was proposed to follow precisely the experimental TGA curve (f vs. T) obtained by a temperature-programed run at heating-up speed $\phi = dT/d\theta$ (θ = reaction time). Assuming the reaction to be first-order with respect to weight of reactive solid, a method based on data-fitting process was derived to determine the rate constant k_ϕ and kinetic parameters (activation energy E and preexponential factor A) of the Arrhenius-type rate constant, from only a single temperature-programed run.

The proposed method was applied to experimental data on the gasification of coal chars with steam and carbon dioxide at temperatures up to 1000°C, and was confirmed to be valid and useful for the quantitative evaluation of kinetic parameters and the comparison of gasification reactivity of coal char.

Introduction

Kinetic models of non-catalytic solid-gas reaction have been reported[4,6] and reviewed by Sestak *et al.*[15] and Hashimoto.[5]

We proposed an isothermal kinetic equation designated as a modified volume reaction model (MVR model).[10,13] We applied this model successfully to experimental data of gasification of different coal chars,[8,11,13] porous pure carbon and activated car-

bon.[10,12] The average rate constant $\bar{k}$ obtained from the isothermal MVR model was found to be a useful measure for quantitative study of the reactivity of coal chars[8,11,13] and of the catalytic effect of mineral matter or ash in coal.[12] However, in an isothermal model, a tedious repetition of experimental runs is required to determine the kinetic parameters such as activation energy E and preexponential factor A in the Arrhenius equation.

The main subject of this work is to propose a kinetic model for temperature-programed thermogravimetry, which makes it possible to obtain an acti-
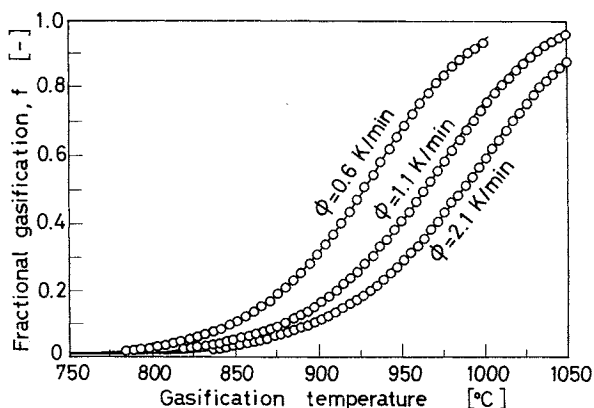
Fig. 1. TGA curves of temperature-programed gasification of Zontagsvlei coal char (av. dia. 1.0 mm; 150 mg) with $CO_2(20\%)$–N_2 mixture. Open circles are the original experimental data points. Solid lines are values calculated by Eq. (3) with the fittest set of parameters.

vation energy and a preexponential factor merely by a single experimental run. This model was applied to the gasification of four kinds of coal chars with steam and carbon dioxide. The kinetic parameters, E and A, determined by use of non-isothermal runs were compared with those by use of conventional isothermal runs. The validity of this model was fully confirmed.

1. Model Equation

1.1 Derivation of equations

In this work, fractional gasification f, which corresponds to fractional weight change of solid sample in general, is based on the initial weight of fixed carbon in coal char (W_0), as defined by Eq. (1).

$$f = 1 - W/W_0 \qquad (1)$$

For non-isothermal runs operated in temperature-programed mode at a heating-up speed of ϕ [K/min], the experimental data are usually presented as a relation between f and temperature T, which is called thermal gravimetric analysis (TGA) curve. Examples are shown in **Fig. 1**.

The reaction rate $-\phi(dW/dT)$ is assumed to be first-order with respect to the weight of remaining fixed carbon (W) at temperature T. Then the rate constant at any point on the curve, k_ϕ [kg/kg (W)·min], is defined by Eq. (2).

$$k_\phi = -\frac{\phi}{W}\left(\frac{dW}{dT}\right) = \frac{\phi}{1-f}\left(\frac{df}{dT}\right) \qquad (2)$$

Here, the next Eq. (3) with three parameters a, b and c is postulated *a priori* to follow precisely the experimental TGA curve derived by the temperature-programing operation.

$$f = 1 - \exp[-a(T-c)^b] \qquad (3)$$

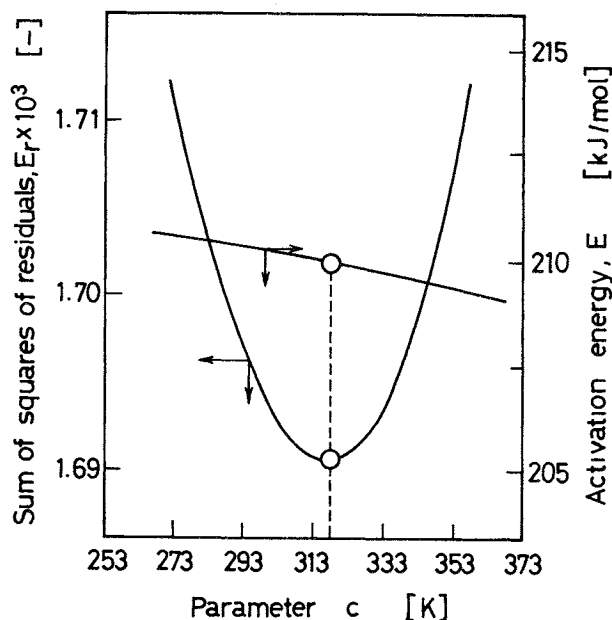Substituting Eq. (3) into Eq. (2), the expression of k_ϕ based on the model Eq. (3) is derived as follows.

Fig. 2. Determination of fittest value of parameter c in Eq. (3) for temperature-programed gasification of Collie coal char (av. dia. 1.0 mm; 200 mg) with $CO_2(20\%)$–N_2 mixture at $\phi = 0.57$ K/min. $c = 318$ K.

$$k_\phi = \phi \cdot ab(T-c)^{(b-1)} \qquad (4)$$

If the reaction satisfies the above assumption, Eq. (4) can be equated to an Arrhenius-type rate constant, $A\exp(-E/RT)$, where E is the activation energy of the reaction and A is the preexponential factor. The kinetic parameters E and A can be determined experimentally by conventional Arrhenius plots according to Eq. (5).

$$\ln k_\phi = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad (5)$$

1.2 Determination of parameters (a, b, c) in Eq. (3)

Precise fitting of Eq. (3) to the experimental TGA curve is the key procedure for application of this non-isothermal model. When a non-isothermal experimental TGA curve is composed of the n-set of data (f_i, T_i), the sum of squares of residuals Er is given by Eq. (6) as a function with the three variables a, b and c.

$$Er = \sum_{i=1}^{n} \{\ln a + b\ln(T_i - c) - \ln[-\ln(1 - f_i)]\}^2 \qquad (6)$$

Equation (6) is not linear, but once parameter c is assumed, Eq. (6) can be reduced to a linear equation, and then the remaining two parameters a and b can be easily determined by the least squares method. By repetition of such trials as assumption of parameter c first and then determination of parameters a and b, the fittest set of parameters can be determined to minimize Er value (see **Fig. 2**).

Table 1. Ultimate and proximate analyses of parent coals

Coal		Native country	Ultimate analysis [wt% daf]					Proximate analysis [wt%, db]			Fuel ratio $(=FC/VM)$ [—]
			C	H	N	S	O_{diff}	VM	FC	ASH	
Ta	Taiheiyo	Japan	75.8	6.5	0.9	0.2	16.7	41.9	41.6	16.6	0.99
Co	Collie	Australia	70.5	4.6	1.4	0.4	23.2	36.4	59.6	4.1	1.64
Z	Zontagsvlei	R. S. Africa	83.9	5.8	2.1	0.6	7.7	30.2	63.4	6.4	2.10
BW	Black Water	Australia	79.4	5.1	2.0	0.4	13.2	27.0	65.6	7.4	2.43

2. Experimental

2.1 Coal char sample

Sample chars were prepared by treatment of four kinds of coals in a nitrogen stream for seven minutes at 1000°C. These parent coals were characterized by ultimate and proximate analyses in detail.[8] The results are summarized in **Table 1**. After sizing to the average diameter, 1.0 mm, a sample char of 150 mg or 200 mg was wrapped in quartz wool and loaded in a skeleton basket (20 mm i.d. × 10 mm height) made of small quartz wire.

2.2 Apparatus and procedure

Experimental apparatus and procedure were almost the same as those reported in the previous paper.[8] Two thermobalance systems (Shimadzu DT-30) were used to measure the weight decrease of the sample char by gasification. One system, equipped with a Pt-heater furnace and an alumina-tube reactor (16.5 mm i.d.), was used for gasification with $CO_2(20\%)-N_2$ mixture up to 1050°C. The other system, equipped with an infrared-ray furnace and a quartz-tube reactor (16.5 mm i.d.), was used for gasification with $H_2O(24\%)-N_2$ mixture up to 900°C. Total flow rate of gasifying agent was 400 Ncm³/min. No effect of total flow rate was found. The non-isothermal gasification was carried out with nominal heating-up speed $\phi = 0.5$, 1 and/or 2 K/min. For comparison, the isothermal gasification was also conducted at several temperatures in the range of 700–900°C.

In this work, the sample char will be identified by the letter/letters in the first column of Table 1.

3. Results and Discussion

3.1 Determination of rate equation

The principal procedure of this method is to express precisely the experimental TGA curve with Eq. (3) as mentioned above. For example, Fig. 1 shows TGA curves of the CO_2-gasification of Zontagsvlei coal char, which was carried out non-isothermally with heating-up speeds of $\phi = 0.60$, 1.1 and 2.1 K/min. The open circles in Fig. 1 indicate the original data points, (f_i, T_i).

A typical example of changes of the sum of squares of residuals Er and the activation energy E are shown
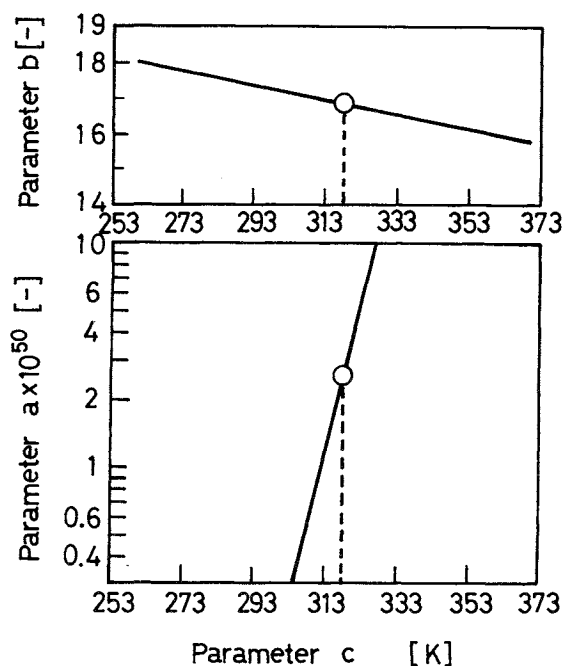

Fig. 3. Changes of parameters a and b with c to give minimum value of Er, shown in Fig. 2. Temperature-programed gasification of Collie coal char (av. dia. 1.0 mm; 200 mg) with $CO_2(20\%)-N_2$ mixture at $\phi = 0.57$ K/min. $a = 2.56 \times 10^{-50}$, $b = 16.8$.

in Fig. 2 as a function of parameter c. The changes of parameters a and b are also shown in **Fig. 3**. The example is the case of the CO_2-gasification of Collie coal char operated with $\phi = 0.57$ K/min, and 30 data points below 1000°C ($f = 0.10–0.79$) were used for calculation. It is clear that Er has a distinct minimum value at c of 318 K, and this point corresponds to the fittest set of parameters a, b and c, and also to the most reliable activation energy E as shown in Fig. 2. It will be noted that the values of b and E do not so strongly depend on the value of c.

All of the solid curves in Fig. 1 superimposed on the original data points were calculated from Eq. (3) after deterimation of parameters a, b and c with data between $T(f=0.05)$ and 1000°C. The rate parameters in Eq. (3) determined for the non-isothermal gasification runs are summarized in **Table 2**. These are usable to reproduce/duplicate the experimental TGA curves with good accuracy, as shown in Fig. 1.

Table 2. Comparisons of kinetic parameters in gasification of coal chars, determined by isothermal and non-isothermal operations

| Operation	Parent coal $\left(\begin{array}{c}\text{Sample char}\\\text{weight}\end{array}\right)$	Isothermal E [kJ/mol]	A [min^{-1}]	Non-isothermal ϕ [K/min]	E [kJ/mol]	A [min^{-1}]	$f = 1 - \exp[-a(T-c)^b]$ a	b	c
CO$_2$(20%)–N$_2$	Collie (200 mg)	201	5.52 × 10^6	0.57	210	1.45 × 10^7	2.56 × 10^{-50}	16.8	318
				1.0	204	7.01 × 10^6	2.32 × 10^{-34}	11.9	564
				2.0	191	1.67 × 10^6	7.95 × 10^{-18}	6.46	846
	Zontagsvlei (150 mg)	215	1.58 × 10^7	0.60	231	9.74 × 10^7	9.94 × 10^{-26}	9.39	757
				1.1	233	1.09 × 10^8	1.26 × 10^{-29}	10.6	708
				2.1	232	1.13 × 10^8	6.04 × 10^{-37}	12.8	592
H$_2$O(24%)–N$_2$	Taiheiyo (200 mg)	141	8.95 × 10^4	0.65	157	4.46 × 10^5	1.45 × 10^{-11}	4.56	847
				1.1	143	1.38 × 10^5	2.97 × 10^{-9}	3.67	875
	Collie (150 mg)	185	5.89 × 10^6	0.64	193	1.13 × 10^7	1.01 × 10^{-21}	8.06	727
				1.1	181	3.76 × 10^6	3.71 × 10^{-17}	6.45	789
				2.2	182	5.25 × 10^6	3.52 × 10^{-38}	13.1	434
	Black Water (150 mg)	226	3.75 × 10^8	0.64	224	2.92 × 10^8	8.63 × 10^{-14}	5.49	897
				0.94	233	5.84 × 10^8	1.35 × 10^{-12}	4.99	925

3.2 Determination of kinetic parameters

Now we know Eq. (4), and the rate constant k_ϕ can be calculated at any point on the TGA curve of temperature, T vs. fractional gasification f.

Examples of the relation between k_ϕ calculated with Eq. (4) and the reciprocals of absolute temperature are the solid lines shown in **Fig. 4**, which are cases of the CO$_2$-gasification of Zontagsvlei coal char shown in Fig. 1. The slope of the line in Fig. 4 is apparently equal to $-E/R$. Though these three experimental runs were to be carried out at different heating-up speeds, Arrhenius plots result in closer lines to each other. It is also obvious that these three lines are almost straight and that their slopes are almost the same. Other examples of Collie coal char, gasified with H$_2$O(24%)–N$_2$ mixture and with CO$_2$(20%)–N$_2$ mixture, are shown and compared in **Fig. 5**. The same remarks are applicable to these cases.

It was found that about 20–30 experimental data points (f_i, T_i), covering $f = 0.05$ to 0.90, sufficed for the analyses of kinetic parameters k_ϕ, or E and A. Values of the activation energy, E and the pre-exponential factor, A, evaluated by applying this procedure are listed in Table 2.

As one of the methods to confirm the validity of this non-isothermal kinetic analysis, isothermal gasification with CO$_2$ and H$_2$O was also carried out under the same conditions except for the temperature operation. For the isothermal run, the average rate constant $\bar{k}$ was calculated by applying the isothermal MVR model equation to the TGA curve, which is shown as the relation between fractional gasification f and gasification time θ. Details of this method were reported in previous papers.[10,13] Open circles in Figs.
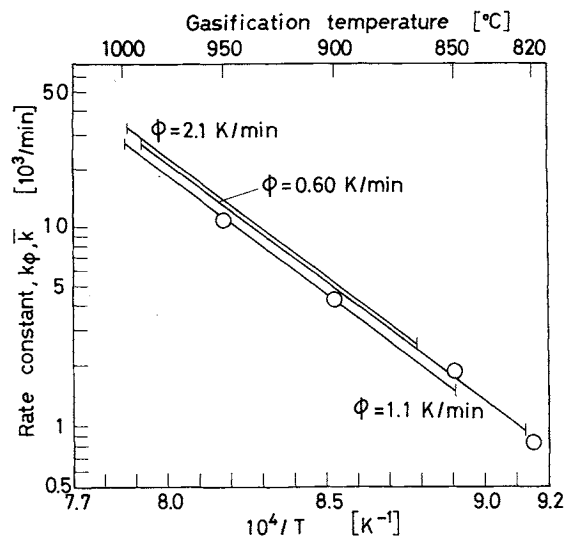
Fig. 4. Arrhenius plots of gasification of Zontagsvlei coal char (av. dia. 1.0 mm; 150 mg) with CO$_2$(20%)–N$_2$ mixture. Solid lines are k_ϕ derived by the non-isothermal runs. Open circles are $\bar{k}$ obtained by the isothermal runs.

4 and 5 indicate the values of $\bar{k}$ determined by the isothermal gasification runs. The kinetic parameters E and A obtained from $\bar{k}$ are listed in Table 2, and are reasonably comparable to those from k_ϕ. However, when it is taken into account that $\bar{k}$ is an average value over $f = 0.01 - 0.99$ and nearly equal to the rate constant at $f = 0.5$ in the isothermal gasification run,[10,13] and that k_ϕ is an usual first-order rate constant in the temperature-programed gasification run, these close coincidences found between k_ϕ and $\bar{k}$ seem to be very suggestive for more advanced understanding of the MVR model equa-
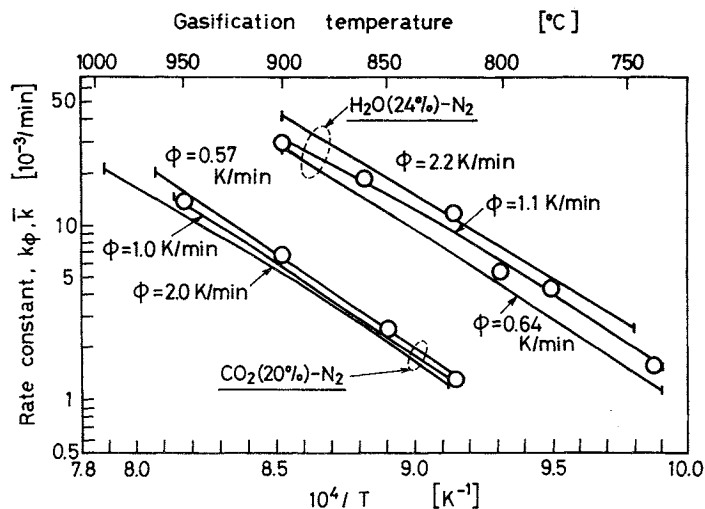
Fig. 5. Arrhenius plots of gasification of Collie coal char (av. dia. 1.0 mm; 200 mg) with $H_2O(24\%)$-N_2 mixture and CO_2 (20%)-N_2 mixture. Solid lines are k_ϕ derived by the non-isothermal runs. Open circles are $\bar{k}$ obtained by the isothermal runs.

tions expressed by Eq. (3).

When a non-isothermal operation is applied to the analysis of kinetic parameters of the reaction, the heating-up speed ϕ to be chosen will strongly depend on the nature of the reaction. In general, a relatively slow heating-up speed is preferable to avoid a temperature lag between sample solid and the point of the temperature detector (i.e. thermocouple) to control the heating furnace. In the gasification of coal char, runs with a heating-up speed $\phi = 1$–2 K/min are recommended in practice.

3.3 Kinetic compensation effect

Values of the kinetic parameters E and A in Table 2 are plotted in **Fig. 6** as the relation between $\log A$ and E. Each of the gasifications with H_2O and CO_2 indicate good kinetic compensation effect.[3,14]

Apparently the lines of CO_2-gasification and H_2O-gasification are in parallel in Fig. 6, but levels of the gasifying agent are different from each other. To compare with the same level of 24%, it was found that a correction of only 0.04 ($= \log\sqrt{24/20}$) should be supplementally added to the value of $\log A$ of gasification with CO_2(20%)-N_2 mixture shown in Fig. 6. This correction was based on our previous finding that $\bar{k}$ is proportional to the square root of the concentration of CO_2 under a similar gasification condition.[8] However, this correction to the CO_2-gasification lines is in practice negligibly small. Therefore, the difference found in these two lines seems attributable to the intrinsic difference in oxidation potential of H_2O and CO_2, but not clear explanation is possible for the lines being in parallel. This speculation is supported by the following findings, shown in **Fig. 7**, of all isothermal runs. In Fig. 7, the data shown with keys of ■ are for H_2O-gasification and ● represents CO_2-gasification. The
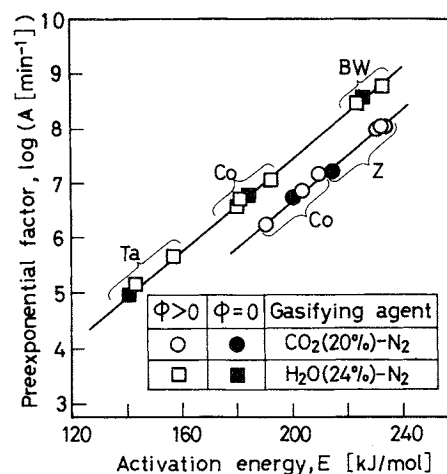

Fig. 6. Compensation effects of kinetic parameters E and A found in gasification of coal chars with $H_2O(24\%)$-N_2 mixture and $CO_2(20\%)$-N_2 mixture. Open marks indicate the non-isothermal runs. Closed marks indicate the isothermal runs.

solid straight lines are the same as those of this work shown in Fig. 6. Our previous data (■)[9] on $H_2O(24\%)$-gasifications of Uonuki coal char (U) and Illinois #6 coal char (I) also just came to be on the line of this work, though carbonization of these coals was carried out in a nitrogen stream for 7 min at 1000°C for Uonuki coal and at 900°C for Illinois #6 coal respectively. In a previous paper,[12] porous pure carbon (PPC), prepared by the thermal decomposition of a synthetic organic resin powder (copolymer of PVDC(70%)-PVC(30%)), was gasified isothermally with $H_2O(24\%)$-N_2 mixture, and the values of $E = 212$ kJ/mol and $A = 9.1 \times 10^7$ min^{-1} were obtained. This is shown as merely PPC in Fig. 7.
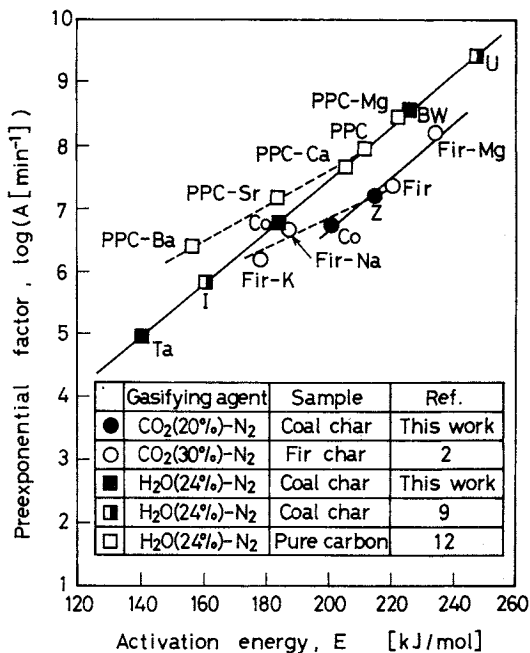
As shown in Fig. 7, the same kinetic compensation

Fig. 7. Comparisons of compensation effects of kinetic parameters E and A obtained in this work with those found in previous works. All runs were carried out isothermally ($\phi=0$).

effects were also found for samples indicated as PPC-Mg and PPC-Ca, but not for samples of PPC-Sr and PPC-Ba, each containing $MgSO_4$, $CaSO_4$, $SrSO_4$ and $BaSO_4$ mixed with porous pure carbon. Only the latter two samples were out of the above pattern, and revealed the effective enhancement in gasification rate and the distinct difference in composition of product gas to be rich in H_2 and CO_2.

DeGroot et al.[2] reported the first-order kinetics of CO_2-gasification of wood (Douglas fir) chars with and without treatments of Na_2CO_3, K_2CO_3 and $Mg(Ac)_2$. The data of ○ keys in Fig. 7 were recalculated from Table 3 of their paper.[2] The untreated fir char and the treated fir-Mg sample showed no catalytic effect on the rate gasification with $CO_2(30\%)$–N_2 mixture, and these two data are very close to the solid line of this work. Other treated samples (fir-Na and fir-K in Fig. 7), exhibiting a significant catalytic effect, were off the solid line. This behavior is quite comparable to that of PPC-Sr and PPC-Ba found in H_2O gasification, as stated above.

All these results also support the validity of the kinetic model for temperature-programed operation as proposed in this paper.

Conclusion

For thermogravimetric analysis of non-catalytic solid-gas reaction, conducted with a temperature-programed operation, an integrated model equation, $f=1-\exp[-a(T-c)^b]$, was proposed to simulate the experimental TGA curve given by the relation be-

tween fractional weight change of solid sample f vs. temperature T. Based on this equation, a procedure to determine activation energy and preexponential factor in the Arrhenius equation from a single-non-isothermal run was also developed.

The proposed methods were applied to the gasification of four kinds of coal chars with mixtures of $CO_2(20\%)$–N_2 and $H_2O(24\%)$–N_2, and were successfully confirmed to be valid by comparison and study of the kinetic parameters obtained from non-isothermal and isothermal runs.[2,9,12] The heating-up speed in the temperature-programed run should be chosen as slow as 1–2 K/min for the coal char gasification.

Both of the kinetic models, that proposed in this paper for non-isothermal run and that reported previously for isothermal run,[10,13] are based on the concept that the overall weight change of the reactive solid (coal char in this work) is the result of reactions taking place in series, parallel and multiple. The true reaction chemistry is undobtedly much more complicated than that implied above.[10,13] Therefore, the kinetic expressions developed in this work are "global" rate equations intended to be useful for numerical modeling or engineering calculations, and must be used to avoid overinterpreting these rate equations in terms of the fundamental microscopic chemistry.

However, model Eq. (3) has been confirmed experimentally to be versatile for any shapes of TGA curves in this work. This method may be a useful tool in many research fields concerning thermogravimetry, especially for the evaluation of gasification reactivity of coal/char.

Nomenclature

A	= preexponential factor defined by Eq. (5)	[min^{-1}]
a	= constant parameter in Eq. (3)	
b	= constant parameter in Eq. (3)	
c	= constant parameter in Eq. (3)	[K]
E	= activation energy for non-catalytic solid-gas reaction, defined by Eq. (5)	[kJ·mol^{-1}]
f	= $1-(W/W_0)$, fractional gasification of coal char, or generally fractional weight change of solid sample	[—]
FC	= fixed carbon by proximate analysis of coal, shown in Table 1	[wt%, db]
FR	= fuel ratio of coal ($=$ a ratio of fixed carbon to volatile matter by proximate analysis of coal)	[—]
k_ϕ	= rate constant, defined by Eq. (2)	[kg·kg(W)$^{-1}$·min^{-1}]
R	= gas constant	[kJ·mol^{-1}·K^{-1}]
T	= reaction temperature	[K]
VM	= volatile matter by proximate analysis of coal, shown in Table 1	[wt%, db]

W	=	residual weight of fixed carbon in coal char at reaction temperature T of temperature-programed run [kg]
W_0	=	initial weight of fixed carbon in coal char sample [kg]
θ	=	reaction time [min]
ϕ	=	heating-up speed of temperature-programed run, $dT/d\theta$ [K·min^{-1}]

⟨Subscript⟩

ϕ	=	non-isothermal, temperature-programed run

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SULPHUR DIOXIDE RETENTION BY CALCINED LIMESTONE UNDER OXYGEN LEAN CONDITIONS

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A kinetic study of sulphur dioxide capture by calcined limestone at 1123 K was conducted by thermogravimetric analysis over a relatively wide range of diameter of limestone particles and concentrations of oxygen as well as sulphur dioxide. The experimental conditions were chosen by taking into consideration the practical operating conditions of a fluidized-bed coal combustor. Results are reported in particular on the effects of oxygen concentration on the rate of sulphur dioxide retention; these effects are of practical importance for staged air firing operation of the bed. A formula which took into account the oxygen and sulphur dioxide concentrations could predict the rate of sulphur dioxide retention at various degree of utilization of sulphur sorbent by defining an approximate maximum utilization level as solid reactivity. This parameter could be expressed by a linearly and monotonously decreasing function of the rate. Detailed effects of particle size on the expression were investigated.

Introduction

Stack emissions from coal-fired boilers are considered to be a major sources of both nitrogen oxides and sulphur dioxide emissions. However, the employment of flue-gas treatment facilities increases construction costs as well as operating costs of power plants and also reduces thermal efficiency.[4]

Thus the fluidized-bed combustion technique is being developed as a prospective alternative to conventional combustion systems. Sulphur dioxide released by combustion can be removed within the bed by limestone fed to the combustor. The combustion temperature is determined to be about the optimum for retention of sulphur dioxide by limestone. The maximum emission level of nitrogen oxides from a fluidized-bed combustor must be reduced to the level projected for the conventional combustion system at the time when fluidized-bed combustion becomes