

Gasification kinetics of five coal chars with CO₂ at elevated pressure

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Abstract—For five coals, the reactivity of char-CO₂ gasification was investigated with a pressurized thermogravimetric analyzer (PTGA) in the temperature range 850-1,000 °C and the total pressure range 0.5-2.0 MPa. The effect of coal rank, initial char characteristics and pressure on the reaction rate were evaluated for five coal chars. The reactivity of low rank coal char was better than that of high rank coal char. It was found that Meso/macro-pores of char markedly affect char reactivity by way of providing channels for diffusion of reactant gas into the reactive surface area. Over the range of tested pressure, the reaction rate is proportional to CO₂ partial pressure and the reaction order ranges from about 0.4 to 0.7 for five chars. Kinetic parameters, based on the shrinking particle model, were obtained for five chars.

Key words: Coal Gasification, IGCC, Gasification Kinetics, Thermogravimetric Analyzer

INTRODUCTION

Coal gasification is a technology that has been widely used in commercial applications for over 40 years in the production of fuels and chemicals. Recently, great attention has been paid for the Integrated Gasification Combined Cycle (IGCC) due to its high efficiency and low pollutants emission. Several commercial IGCC plants for power generation are being developed worldwide. Since the coal gasifier of IGCC is operated at elevated pressure and high temperature, it is important to obtain characteristics of coal gasification under the same gasifier conditions. These characteristics are dependent on the coal type and operating conditions.

The gasification of coal consists of two consecutive steps: (1) devolatilization of coal to produce char, gases, and tar, and (2) the gasification of the char produced. Since the rate of the second step is much slower than that of the first step, the design and operating conditions depend on the gasification rate of char. However, there have been few studies on char reactivity at high pressure [Goyal et al., 1989; Kuhl et al., 1992; Shufen and Ruizheng, 1994; Liu et al., 2000; Ahn et al., 2001 and Kajitani et al., 2002]. Among the char-gas reactions in a coal gasifier, the char-CO₂ reaction is considered to be one of the rate limiting reactions since the reaction is endothermic and the rate is relatively slow.

In this study, a pressurized thermogravimetric analyzer (PTGA) was used to study kinetics of the char-CO₂ reaction at elevated pressures up to 2.0 MPa and temperatures between 850 and 1,000 °C. The objectives of this study were to investigate the effects of coal rank, partial pressure and total pressure on the char-CO₂ reaction. Five coals, imported in the South Korea, were used and their kinetic parameters were obtained.

EXPERIMENTAL

1. Experimental Apparatus and Analyzers

Reactivities of char samples were measured with a pressurized

thermogravimetric analyzer (PTGA). The Chan TG 151 employed in this study can operate up to a temperature of 1,100 °C and pressure of 10 MPa. A schematic diagram of PTGA system is shown in Fig. 1. The reaction tube, made of quartz tube (34 mm in inside diameter), is surrounded by heating elements contained in a pressure vessel. The reaction gases (N₂ or CO₂) are passing through this

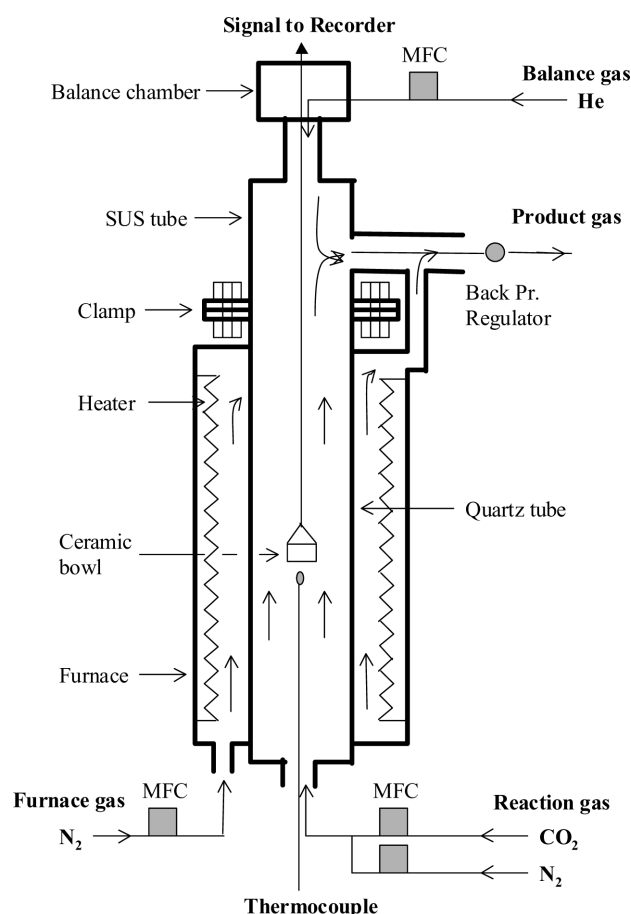


Fig. 1. A schematic diagram of PTGA system.

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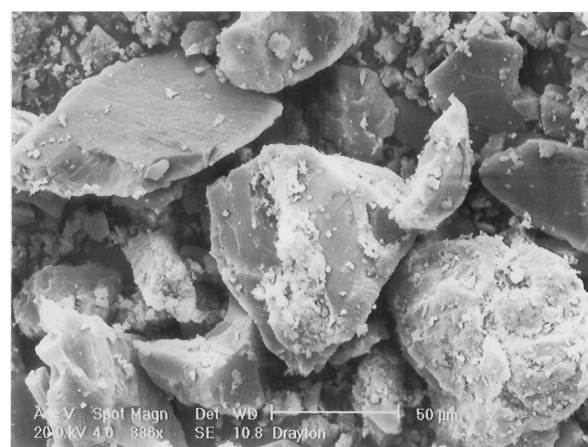
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tube, while the furnace gas (N₂) is flowing outside of this tube. The balance gas (He) is supplied to the balance chamber and goes to the reaction tube. In the pressure control section, all three gases are mixed together. Each mass flow controller (MFC) regulates the flow rates of corresponding gases. The back-pressure regulator controls the system pressure at the outlet of the furnace. The char sample was placed in a ceramic bowl (10 mm in diameter and 3 mm in height) which was connected to the balance, and its temperature was monitored with a thermocouple just below the ceramic bowl.

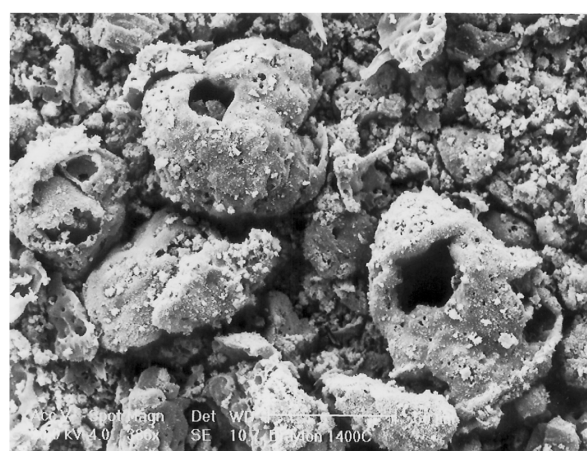
For characterizing char structure, an ASAP 2405 (Micromeritics) was employed to determine N₂ surface area of char from the BET equation. Nitrogen adsorption isotherms at 77 K were followed up to a relative pressure value of 0.35, and an effective cross-sectional area of 0.162 nm² was assumed for the N₂ molecule. A mercury porosimeter (Autopore III 9420, Micromeritics) was used to obtain mercury densities. The surface tension of mercury and the contact angle were assumed to be 0.485 Nm⁻¹ and 130°, respectively. Helium density was obtained from helium pycnometry. Helium penetrates the micropores, but some of the pores may be blocked to helium; thus, this helium density is only an approximation of the true solid density. Char samples of about 3-4 g were used to obtain reliable true density. An Accupyc 1330 (Micromeritics) was used.

2. Char Preparation

In this study, five coals (Alaska, Cyprus, Drayton, CNCIEC and Denisovsky) were selected to investigate the effect of coal rank on the gasification kinetics; they range from sub-bituminous coal (Alaska) to low volatile bituminous coal (Denisovsky). The selection of coal used was based on the carbon in dry-ash free basis and ratio of volatile to fixed carbon (VM/FC) of the parent coal. Char samples were prepared in a pressurized drop tube furnace (PDTF). The proximate and ultimate analyses of coals and chars are presented in Table 1. Coal was introduced into the furnace and devolatilized in nitrogen at atmospheric pressure, a heating rate of about 10⁴ K/s and residence time of about 0.6 sec. Gas temperatures along the furnace were controlled to 1,400 °C with three segmental heating elements. These devolatilization conditions were chosen to simulate the devolatilization process occurring in a gasifier. A temperature of 1,400 °C



(a)



(b)

Fig. 2. (a) Photograph of parent Denisovsky coal, (b) Photograph of Denisovsky coal char.

can ensure complete devolatilization. Coals were initially ground and sieved in the range of 45-63 μm in diameter. After devolatil-

Table 1. Analyses of parent coals and chars

Type	Ultimate analysis (wt%, daf)					Proximate analysis (wt%, dry)			
Coal	C	H	O	N	S	Moisture	VM ^a	Ash	FC ^b
Alaska	73.47	5.65	19.86	0.87	0.16	4.87	45.82	4.1	45.21
Cyprus	75.01	5.31	18.24	1.18	0.25	4.46	42.27	5.24	48.03
Drayton	78.22	5.37	14.08	1.75	0.59	1.71	29.9	24.69	43.7
Denisovsky	85.06	5.26	8.04	1.26	0.38	1.8	25.72	12.65	59.83
CNCIEC	89.07	5.00	4.08	0.99	0.86	2.74	25.32	11.31	60.65
Char	C	H	O	N	S	Moisture	VM	Ash	FC
Alaska	97.89	0.42	0.40	1.10	0.19	2.20	7.78	10.75	79.27
Cyprus	97.28	0.43	0.83	1.19	0.26	1.33	8.59	12.22	77.86
Drayton	86.96	0.97	10.71	1.17	0.19	1.49	13.78	35.59	49.14
Denisovsky	98.07	0.36	0.31	0.89	0.36	0.83	4.78	19.92	74.47
CNCIEC	98.04	0.73	0.09	0.96	0.18	0.46	6.86	14.89	77.85

^aVM: Volatile matter

^bFC: Fixed carbon

ization, chars collected in a cyclone and dust filter were again sieved to sizes of 45–63 μm in diameter. A detailed description of PDTF and char preparation was given in Ahn et al. [2001]. Fig. 2(a) and (b) show the photographs of Scanning Electron Microscopy (SEM) of raw Denisovsky coal and char obtained from the PDTF, respectively. SEM has revealed irregular sharp edged shape of coal particles, as seen in Fig. 2(a). Generally, as the coal particles undergo devolatilization in the form of many jets issuing from the parent coal, many blow-holes are created on the coal particles, and char particles are produced [Kang et al., 1988]. Fig. 2(b) shows the char particles to have some rough, spherical, irregular and rounded edges with small pores on the surface.

3. Char Gasification

After about 10 mg of char sample was placed in a ceramic bowl, the PTGA system was pressurized to the desired pressure by supplying N_2 for both reaction and furnace gas, and He for balance gas at the respective flow rate. After good pressure control was confirmed at the desired system pressure, the reaction temperature was increased to the experimental value at a heating rate of 20 $^\circ\text{C}/\text{min}$. With a settling time of 20 min, a certain amount of reactive gas (CO_2) was introduced into the reaction tube and simultaneous decrease of N_2 was followed. Finally, experimental CO_2 and N_2 concentrations were adjusted with mass flow controllers. During the reaction, the mass loss, rate of mass loss, sample temperature, and system pressure were recorded by system software in a preset time interval.

The carbon conversion (x) and the reaction rate (dx/dt) were evaluated on the basis of the initial weight of char sample. The conversion is defined as:

$$x = \frac{(W_0 - W)}{(W_0 - W_{ash})} \quad (1)$$

where W_0 , W and W_{ash} represent the initial weight of char, the instantaneous weight of char and the weight of ash, respectively. The weight

of ash was assumed to be the proximate analysis of char.

The reaction rate (min^{-1}) was calculated by using the following equation:

$$\frac{dx}{dt} = - \frac{dW}{dt} \frac{1}{(W_0 - W_{ash})} \quad (2)$$

High pressure and temperature have some effects on the PTGA reading. Weight loss occurs during pressurization, while weight gain occurs during temperature rise. These result from the buoyancy effect [Brown et al., 1972]. This effect was negligible in the present isothermal experiment since the temperature and pressure were kept constant during the reaction and the change in sample volume was little. Also, the reaction gas velocity should be constant since it affects the weight recording through an aerodynamic drag force on the ceramic bowl. The gas velocity in the present study was maintained to be constant by varying the flow rate of reaction gas at each experimental condition. The measured weight data showed small oscillations under high pressure. Smooth weight data were reproduced by the PTGA system software, and used to calculate the conversion and reaction rate.

The effect of initial weight of char sample on the reaction rate was examined by varying the sample weight from 7 to 20 mg. For pressurized isothermal tests (1.0 MPa and 900 $^\circ\text{C}$), the reaction gas was supplied to the reaction tube at a flow rate of 1,300 ml/min. At this condition, the measured reaction rate of Alaska char was relatively constant with the initial weight of char in the range 7–13 mg. It implied that the effect of diffusion on the sample was small. Therefore, all experiments were carried out with a char sample of about 10 mg. When the total pressure was varied with experimental condition, the flow rate of reaction gas was adjusted on the basis of this condition in order to maintain constant gas velocity in the reaction tube.

Considering an operating condition of commercial gasifier, exper-

Table 2. Experimental conditions of char- CO_2 gasification in PTGA

At total pressure of 1.0 MPa and reaction temperature of 900 $^\circ\text{C}$				
CO_2 partial pressure (MPa)	0.180	0.256	0.417	0.495
At partial pressure of 0.287 MPa and reaction temperature of 900 $^\circ\text{C}$				
Total pressure (MPa)	0.5	1.0	1.5	2.0
At total pressure of 1.0 MPa and CO_2 partial pressure of 0.256 MPa				
Reaction temperature ($^\circ\text{C}$)	850	900	950	1000

Table 3. Characteristics of chars

Char samples	Parent coal		Helium density	Apparent density	Mercury density	Open porosity	Pore volume (ml/g)			Surface area (m^2/g)	
	C_{daf} (wt%)	VM/FC	ρ_{He} (g/ml)	ρ_a (g/ml)	ρ_{Hg} (g/ml)	P (-)	Total	Macro & Mesopore	Micro pore	N_2 BET	CO_2^a
Alaska	73.47	1.01	2.22	0.48	0.87	0.79	1.65	0.96	0.69	188.16	319.75
Cyprus	75.01	0.88	2.14	0.43	0.84	0.80	1.87	1.15	0.72	178.99	290.61
Drayton	78.22	0.68	2.16	0.69	1.06	0.68	0.98	0.50	0.48	24.80	247.83
Denisovsky	85.06	0.43	2.00	0.55	0.88	0.73	1.32	0.68	0.64	37.91	192.29
CNCIEC	89.07	0.42	1.68	0.64	1.09	0.62	0.98	0.66	0.32	23.00	190.13

^aThese were calculated from correlation, $S_0 = 218.4 \times (\text{VM/FC}) + 98.4$ [14].

imental conditions for char-CO₂ reaction are determined as Table 2, which vary from 0.5 to 2.0 MPa in total pressure, 850 to 1,000 °C in reaction temperature and 0.18 to 0.495 MPa in CO₂ partial pressure.

RESULTS AND DISCUSSION

1. Char Characteristics

The physical characteristics of the chars are given in Table 3. The apparent density of the chars, ρ_a (g/ml), was measured with mercury intrusion at 413 kPa assuming that the inter-particle voids and intra-particle voids with openings larger than 3.7 μ m are excluded in the intrusion volume [Ng et al., 1988; White et al., 1991]. In this study, the char particle density obtained by mercury porosimetry was designated as a mercury density, ρ_{Hg} (g/ml). It was the density measurement of particle with the solid plus pores below 4.6 nm in diameter, and measured at 343.7 MPa. Open porosity, P (%), defined as the percentage of total volume of open pores relative to the char volume, was calculated with the apparent density, ρ_a (g/ml), and helium density, ρ_{He} (g/ml). The total pore volume, V_T (ml/g), and micropore volume below 4.6 nm in pore diameter, V_{mi} (ml/g), could also be determined by the combination of helium, apparent and mercury densities. These are calculated with the following equations:

$$P = \left(1 - \frac{\rho_a}{\rho_{He}}\right) \quad (3)$$

$$V_T = \frac{1}{\rho_a} - \frac{1}{\rho_{He}} \quad (4)$$

$$V_{mi} = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \quad (5)$$

Comparing open porosities and pore volumes in Table 3, Alaska and Cyprus char are more porous than other chars are. As the rank of the parent coals increases, both the open porosity and pore volumes of the chars decrease (Fig. 3). It was due to that, during the devolatilization process, more pores were generated with the low rank coals containing high volatile matters. Open porosities in Table 3 give higher values than those obtained by other researchers [Ng et al., 1988; Fernandez-Moorales et al., 1985; Sahu et al., 1988]. Their devolatilization conditions for preparing char were slower in heating rates and lower in devolatilization temperature than those of this study. It is likely that the severer devolatilization produced more

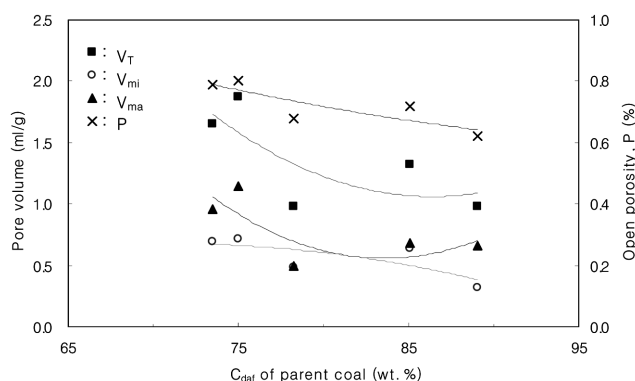


Fig. 3. Variations of open porosity and pore volumes with carbon content of parent coal.

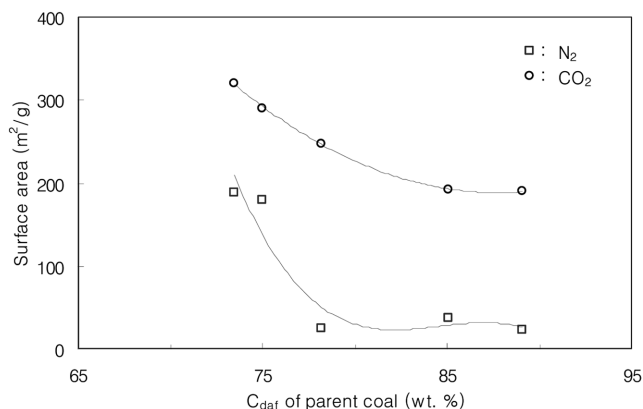


Fig. 4. Relationship between surface area and carbon content of parent coal.

volatiles and more pores resulted from the escape of more volatiles from the particle interior to the ambient atmosphere. The higher portion of macro and mesopores (4.6 nm < pore diameter < 3.7 μ m) in total pore volume than that of micro pore volume (pore diameter < 4.6 nm) are common in five chars, indicating that the macropores were well developed in those chars. It has been known that the level of macro and mesopore markedly affects reactivity since these pores provide channels for diffusion of reactant gas into the micropores [Jenkins et al., 1973; Fernandez-Moorales et al., 1985]. In micropore volume, Alaska and Cyprus char also have higher values, compared to those in other chars.

Surface area data are also summarized in Table 3 and in Fig. 4. The CO₂ surface area in Table 3 was predicted from the correlation between surface area and ratio of volatile matter (VM) and fixed carbon (FC) in the parent coal [Liu et al., 2000]. The CO₂ surface areas of Alaska and Cyprus char are about 1.7 times larger than the corresponding N₂ surface area. On the whole, 5-10 times larger CO₂ surface areas than N₂ surface areas are found in Drayton, Denisovsky and CNCIEC char. It has been known that N₂ surface area is relevant to relatively larger pores, and CO₂ surface area represents the total surface area. Also, most surface area is in micropores as has been reported [Ng et al., 1988; White et al., 1991; Dutta et al., 1977]. Therefore, it can be concluded that the contribution of micropores to CO₂ surface area is pronounced in Drayton, Denisovsky and CNCIEC chars. For Alaska and Cyprus chars, a considerable portion of CO₂ surface area is attributed to meso and macropores.

Fig. 4 shows a comparison of the N₂ and CO₂ surface area with C_{daf} (wt%) of the parent coal. The chars up to 78% in C_{daf} (wt%) have much larger N₂ surface area. Beyond that, the N₂ surface areas of chars are small and comparable. On the whole, the CO₂ surface area continuously decreases with C_{daf} (wt%) of the parent coal. As seen in Fig. 4, the N₂ surface area gives a relative dependency on coal rank. However, a better correlation is obtained between the CO₂ surface area and C_{daf} (wt%) of the parent coal.

2. Effects of Coal Rank on Reaction Rate

For five chars, the conversion (x) versus time (t) and the reaction rates (dx/dt) versus conversion (x) are shown in Fig. 5(a) and (b), respectively. These were obtained at temperature of 900 °C, CO₂ partial pressure of 0.256 MPa, and total pressure of 1.0 MPa. The reaction rates increase during the initial stage of conversion and reach

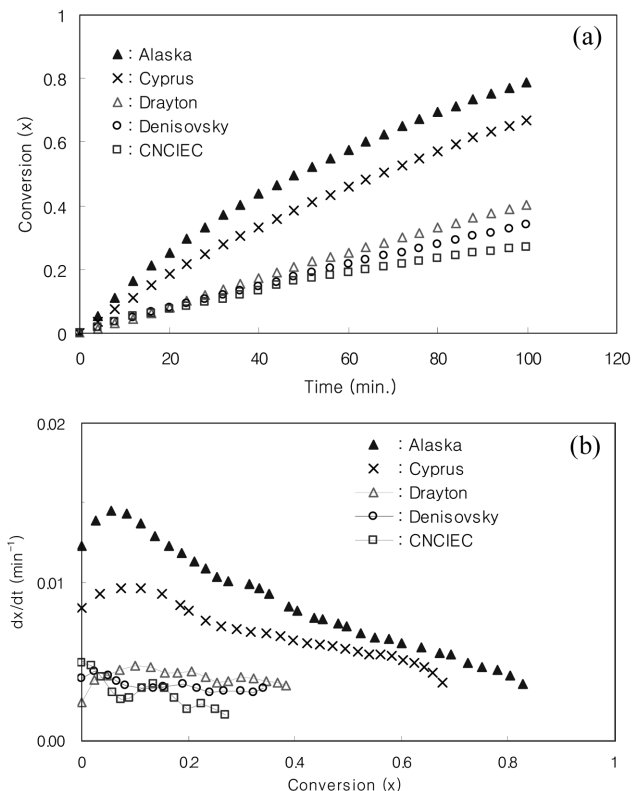


Fig. 5. (a) Conversion as a function of time for five chars, (b) Measured reaction rate as a function of carbon conversion for five chars

a maximum value at around 10% conversion; then the rates decrease. These curves are very similar to those given by Liu et al. [2000], who performed a PTGA test at pressurized conditions. Generally, enlargement of existing pores occurs during the initial stage of reaction and results in an increase of surface area. As the reaction proceeds, pores in the char are merged and developed further so that the surface area decreases. The reaction rate presents a maximum value, as does the surface area, for conversion between 20 and 60% [Molina and Mondragon, 1998]. However, in the present experiment, the maximum rate presents around 10% conversion. It might be that sufficient pore development during high temperature (1,400 °C) devolatilization seldom gives the opportunity of initial pore development. It has been reported that the property of devolatilization products (char, gas tar and other material) is a function of the structure and composition of the coal as well as the reaction condition (temperature, heating rate, residence time, pressure and gas atmosphere) [Song et al., 2001].

The maximum rate, $(dx/dt)_{max}$, and the initial rate, $(dx/dt)_{x=0}$, are presented in Fig. 6 as a function of C_{daf} (wt%) of the parent coal. The maximum rate and initial rate have been widely used in literature [Jenkins et al., 1973; Hashimoto et al., 1986; Kajitani et al., 2002]. Fig. 6 shows that Alaska and Cyprus chars are two or three times more reactive than other chars. When plotting $(dx/dt)_{max}$ and $(dx/dt)_{x=0}$ against (VM/FC) of the parent coal, we obtained the same results. It has been reported that char reactivity decreases as coal rank increases, even scattered in low rank coal [Miura et al., 1989; Fung and Kim, 1990]. The same observation is obtained in the present

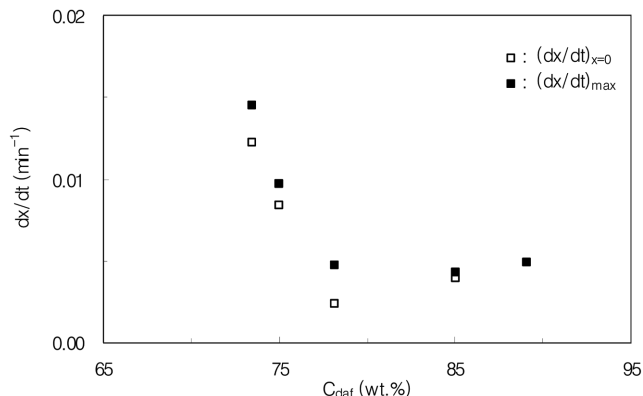


Fig. 6. Measured reaction rates as a function of carbon content of parent coal.

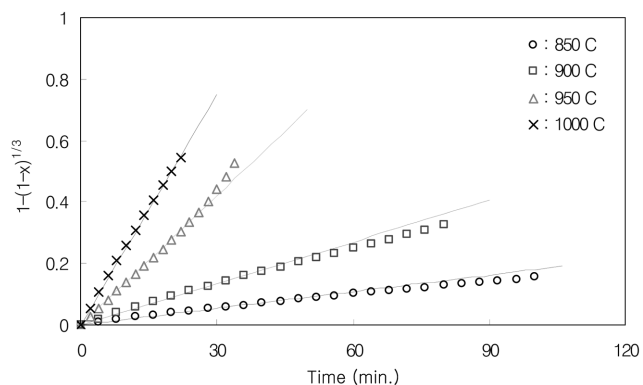


Fig. 7. Relationship of $1-(1-x)^{1/3}$ with t for Alaska char.

study although a small range of coal was tested.

3. A Fitting of Reaction Model

The simple and widely used model for char- CO_2 reaction is the shrinking particle model. When the rates of diffusion through a fluid-film and a porous solid are both fast, the overall rate of a solid-fluid reaction is entirely controlled by the inherent chemical reactivity of the solid reactant [Fung and Kim, 1990]. Reaction rate and conversion for the particle model are expressed as follows:

$$\frac{dx}{dt} = k_g(1-x)^{2/3} \quad (6)$$

$$x = 1 - \left(1 - \frac{1}{3}k_g t\right)^3 \quad (7)$$

where k_g (min⁻¹) the surface reaction rate constant. The rate constants, k_g , are expressed as an Arrhenius type with the reaction order (n) which represents the effect of partial pressure of reactant gas:

$$k_v, k_g = A P_{CO_2}^n \exp\left(-\frac{E}{RT}\right) \quad (8)$$

where A (min⁻¹ MPa⁻ⁿ) is the pre-exponential factor, E the activation energy (kJmol⁻¹), R the gas constant (8.314 J mol⁻¹ K⁻¹), and T the reaction temperature.

The relationships between conversion (x) and reaction time (t) can be obtained from Eq. (7):

$$1 - (1 - x)^{1/3} = \frac{1}{3} k_g t \quad (9)$$

Fig. 7 shows plots of $1 - (1 - x)^{1/3}$ versus reaction time (t) for Alaska char at different temperatures. This gasification test was performed at total system pressure of 1.0 MPa and CO₂ partial pressure of 0.256 MPa. The slope of straight lines in Fig. 7 provides the values of rate constants, k_g . Good linearities are obtained with the shrinking particle model. From an overall point of view for five chars, the better agreement (linear plots) occurs with the shrinking particle model. This coincides with the result of Shufen and Ruizheng [1994], who reported that the shrinking particle model gave good agreements with experimental data for char gasification with CO₂ and H₂O at 1.96 MPa.

At total pressure of 1.0 MPa and CO₂ partial pressure of 0.256 MPa, the obtained rate constants, k_g , of five chars are given in Fig. 8. Alaska char has four or five times higher value in rate constant than that of Denisovsky char.

4. Effects of Pressure on Reaction Rate

The effect of partial pressure on reaction rate was tested by varying CO₂ partial pressure from 0.18 to 0.495 MPa at 900 °C and total pressure of 1.0 MPa. The obtained rate constants, k_g , versus partial pressure are shown in Fig. 9. In the ranges of tested CO₂ partial pressure, the reaction rate constants for five chars are proportional to CO₂ partial pressure, and found to be values of about 0.4-0.7 for the reaction order. Dutta et al. [1977] reported that the reaction order of char-CO₂ gasification converged to zero for high pressure (above

15 atm), while the reaction order converged to 1.0 for low pressure (below atmosphere).

The present results show that the reaction order for low volatile coal char gives a higher value (0.697), while for high volatile coal char a lower value (0.397) is given. For lignite char, Shufen and Ruizhang [1994] found the reaction order to be 0.34 for CO₂ gasification at pressure of 1.6 MPa and temperatures 800-900 °C. The low rank coal char seems to be less affected by reactant gas pressure than the high rank coal char.

The effect of total pressure on CO₂ gasification rate was also studied at CO₂ partial pressure of 0.287 MPa and temperature of 900 °C. The total pressure was varied from 0.5 MPa to 2.0 MPa. Fig. 10 shows the rate constants, k_g , versus total pressure for three chars. Minor variations in rate constants are observed at a given total pressure range. This result is in agreement with the results reported by Goyal et al. [1989]. Their experimental results showed that, for char gasification with steam-hydrogen mixture, the difference in the values of rate constants between runs conducted at 14 and 28 atm was very small. Their experiments were performed with a high-pressure thermo-balance under chemically controlled reaction regime.

5. Activation Energy and Frequency Factor

Parameters (E and A) of rate constants (k_g) for five chars were obtained from the Arrhenius plots in the temperature range 850-1,000 °C. Arrhenius plots are shown in Fig. 11 and the obtained kinetic parameters are given in Table 4. Parameters range from 149 to 223 kJ/mol for activation energy, 5.17×10^4 - 1.05×10^6 (min⁻¹MPa⁻¹)

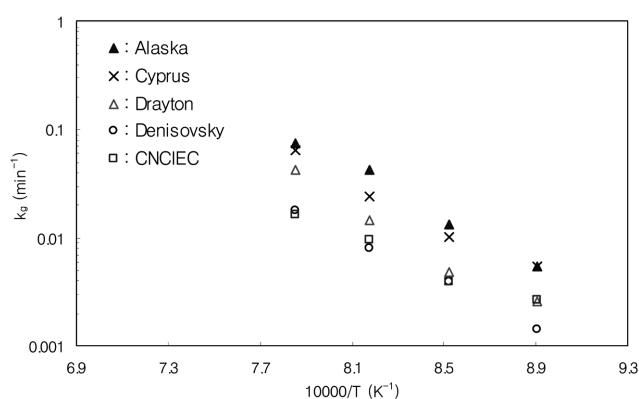


Fig. 8. Rate constants for five chars at various temperatures.

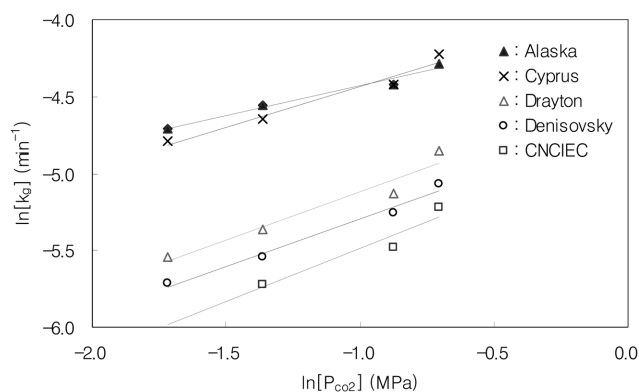


Fig. 9. Rate constants, k_g , versus partial pressure for five chars.

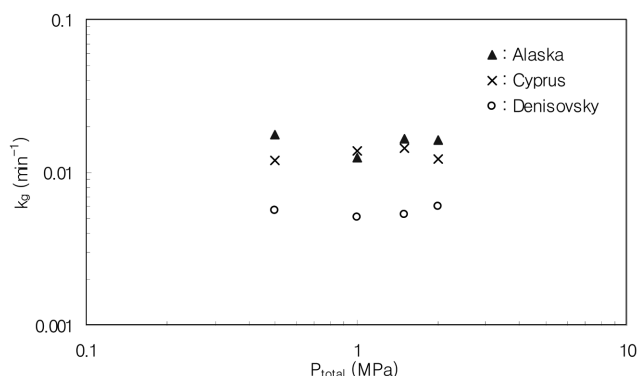


Fig. 10. Effect of total pressure on reaction rate constants, k_g , for three chars.

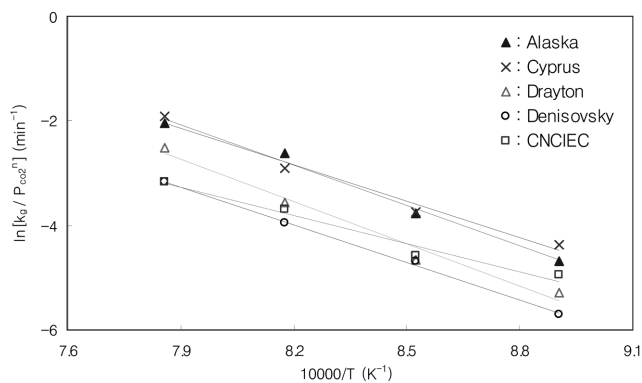


Fig. 11. Arrhenius plots for CO₂ gasification with five chars.

Table 4. Kinetic parameters for CO₂ gasification with five chars

Char	Reaction order (n)	E (kJ mol ⁻¹)	A (min ⁻¹ MPa ⁻¹)
Alaska	0.397	215	9.37E+07
Cyprus	0.610	194	1.22E+07
Drayton	0.488	223	1.05E+08
CNCIEC	0.697	149	5.17E+04
Denisovsky	0.622	199	6.31E+06

for frequency factor. Shufen and Ruizheng [1994] obtained activation energy of 149.1 kJ/mol at 1.96 MPa. Ahn et al. [2001] obtained activation energy of 144 kJ/mol for Indonesian Roto coal char. The present values for activation energy are compatible with those obtained by other researchers.

CONCLUSIONS

For five coal chars prepared under the same devolatilization conditions, CO₂ gasification tests were carried out using PTGA at total pressures from 0.5 to 2.0 MPa and in the temperature range 850–1,000 °C. The gasification reactivity of the char is affected by the rank of parent coal. The char reactivity increases as coal rank decreases, with comparable variations in high rank coal chars. It is concluded that meso/macro-pores of char markedly affect char reactivity by way of providing channels for diffusion of reactant gas into the reactive surface area.

For five chars tested in this study, the shrinking particle model gives reasonable agreement with experimental data for char gasification with CO₂ at various conditions. With this model, the obtained parameters of rate constants range from 149 to 223 kJ/mol for activation energy, 5.17×10^4 to 1.05×10^8 (min⁻¹MPa⁻¹) for frequency factor.

In the range of tested CO₂ partial pressure (0.18–0.495 MPa), the reaction rates for five chars are proportional to CO₂ partial pressure, and found to be values of about 0.4–0.7 for the reaction order.

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