Research Article

Measurements of Gasification Characteristics of Coal and Char in CO₂-Rich Gas Flow by TG-DTA

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Pyrolysis, combustion, and gasification properties of pulverized coal and char in CO₂-rich gas flow were investigated by using gravimetric-differential thermal analysis (TG-DTA) with changing O₂%, heating temperature gradient, and flow rate of CO₂-rich gases provided. Together with TG-DTA, flue gas generated from the heated coal, such as CO, CO₂, and hydrocarbons (HCs), was analyzed simultaneously on the heating process. The optimum O₂% in CO₂-rich gas for combustion and gasification of coal or char was discussed by analyzing flue gas with changing O₂ from 0 to 5%. The experimental results indicate that O₂% has an especially large effect on carbon oxidation at temperature less than 1100°C, and lower O₂ concentration promotes gasification reaction by producing CO gas over 1100°C in temperature. The TG-DTA results with gas analyses have presented basic reference data that show the effects of O₂ concentration and heating rate on coal physical and chemical behaviors for the expected technologies on coal gasification in CO₂-rich gas and oxygen combustion and underground coal gasification.

1. Introduction

As the increased fossil fuels consumption such as coal, oil, and gas leads to rapid deterioration of global environment, nowadays low-carbon economy is getting more and more attention. Low-carbon economy mostly linked greenhouse gases emissions and energy usage together [1, 2]. The economic growth of energy consumption countries impels intensive use of energy and other natural resources; thus, more residues and wastes discharged in the nature lead to environmental aggravation. China has been the second largest energy consumption country in the world, where the total energy consumption increased from 302 million tons of standard coal equivalent in 1960 to 2850 million tons in 2008 [3]. Coal as an energy source plays an important and indispensable role on future energy mix due to its proven stability in supply and its low cost. Coal has improved its long-term position as the world's most widely available fossil energy source with a very large resource base and economically recoverable reserves that are much greater than those of oil and gas. Coal is the most abundant fossil fuel in China.

Present recoverable reserves occupied about 11.67% of global coal reserves based on Key World Energy Statistics 2010 [4], ranked third in the world, with potential total reserves far in excess of this amount. Chinese coal consumption by the year 2020 will be nearly 4.8 billion tons per year with the bulk being consumed through the combustion processes. Therefore, present recoverable reserves are adequate to meet the national coal needs for many decades and potentially much longer. Moreover, most of coal consumptions are for electric power generations, with industrial consumptions of coal for steam and heat and for chemical and metallurgical processes being other major uses [5].

Carbon dioxide (CO₂) is regarded to be the main source of greenhouse gases emission that is a major threat of global warming and climate change [6]. According to the Intergovernmental Panel on Climate Change (IPCC), approximately 75% of the increase in atmospheric CO₂ is attributable to the consumption of fossil fuels [7, 8]. According to statistics of the IEA (2011) [9], CO₂ emission from fossil energy consumption in China was accounted for about 19% of global CO₂ emission, of which coal-fired power plants occupied

FIGURE 1: Schematic diagram of three kinds of power generation with CO₂ capture.

about 52.6% of total CO₂ emission in China. International Energy Agency (IEA) predicted that in 2030 China would emit twice as much carbon dioxide as that in 2007, provided that CO₂ emissions increase by 2.9% each year [10].

As stationary sources emitting large amounts of CO₂, pulverized coal fired power plants could be the best candidates to install CO₂ capture system which can be classified into three categories in general: precombustion capture, postcombustion capture, and oxy-fuel strategy as shown in Figure 1 [11, 12]. The traditional coal fired boilers use air for combustion in which N₂ gas is 79% in volume ratio. Its flue gas includes only about 15% CO₂; therefore, the CO₂ capture efficiency by post-combustion system is not high [13, 14]. Furthermore, CO₂ capture cost from the flue gas using amine scrubbing is expected to be relatively high [15]. In the case of pre-combustion capture, although calorific value of oxy-fired coal boiler is higher than that of air-fired coal boiler, there is a major disadvantage for oxygen-blown gasifier that is to build an oxygen plant. In general, an oxygen plant consumes about 5% of the gross power generated, which is the main reason why the total of plant investment for an oxygen-blown plant is somewhat higher than that of an air-blown plant [5].

As an alternative, a zero-emission power plant of pulverized coal-fired power generation in a nitrogen-free atmosphere, most known as oxy-fuel or O₂/CO₂ combustion technology for pre-combustion capture, is one of new promising methods to approach the problem of CO₂ separation and capture. In this technology, CO₂ gas substitutes the role of O₂ gas to improve and stimulate coal conversion and reduce O₂ consumption. Recently, coal gasification with CO₂ and oxygen combustion technology has been investigated for next coal fired power [16, 17]. In addition, this type of pulverized coal fired power plant is mainly composed of gasifier and combustor as shown in Figure 1. Moreover, gasification process of pulverized coal in the gasifier is the core part of the technology because it determines synthesis gas product and thermal efficiency. This process is also the

focus of the research in this paper; moreover, it has been verified that the processes of coal in CO₂-rich gas atmosphere mainly are divided into two temperature ranges for coal devolatilization, char formation, and gasification.

The implementation of these improved combustion technologies for replacing N₂ with CO₂ in feeding gas requires further understanding of physical and chemical characteristics in the process of oxidation combustion and gasification of coal with gradually increasing temperature in CO₂-rich atmosphere. In particular, reaction characteristics of coal gasification in a CO₂-rich atmosphere are required for coal seam underground coal gasification (UCG) projects. Li et al. presented the comparisons in TGA experiments with bituminous coal at high temperature of 1000°C with heating rate of 10 to 30°C·min⁻¹ in the mixture of O₂/N₂ or O₂/CO₂ with various oxygen concentrations (21, 30, 40, and 80%) [18], and Liu presented the properties of coal chars prepared from UK high-volatile bituminous and anthracite coals by using TGA with heating rate of 2.5 to 12.5°C·min⁻¹ in mixtures of O₂/CO₂ and O₂/N₂ with O₂ concentrations of 3, 6, 10, 21, and 30% [19]. However, researchers did not measure flue gas and heat generation by coal combustion and gasification. The unburned carbon content in CO₂ rich atmosphere is expected to be higher than those in air environment due to O₂ concentration.

Authors (Li et al., 2012) [20] have presented the combustion and gasification properties of Datong coal and char in CO₂-rich gas flow (5 or 10% O₂) by rapid heating with temperature gradient of 50 to 200°C·s⁻¹ using a CO₂ laser beam. In the experiments, the coal conversion ratio to gases was measured for different coal temperature time gradient with monitoring of CO and HC gases generated from heated coal particles. Based on experimental results by the rapid heating of dry, moist coal, and mixing coal-water samples, it has been clarified that coal moisture (internal water) and external water of coal particles have the same function to increase HC-gas production and decrease CO-gas amount by promoting chemical reactions between carbon or CO and H₂O. Consequently, a possibility has been shown to accomplish coal gasification in CO₂-rich atmosphere including enough water vapor to carry out low-cost CO₂ capture.

Most researchers presented the results in TGA experiments with coal and char at high temperature; however, the experimental results were restricted to HCs and CO gasified gases analysis and heat generation after coal gasification. Investigation of gasification and combustion reactivity of coal in CO₂-rich atmosphere at high temperature, HCs, CO, and so forth gasified gases generations is essential for the development of gasification technology in the future. In contrast with gasification furnace in commercial process, pyrolysis, combustion, and gasification properties of pulverized bituminous coal were investigated at high temperature of 1400°C by TG-DTA measurements. On the other hand, temperature gradient was set up from 20 to 40°C·min⁻¹ in order to discuss gasification and combustion ratio of coal conversion. In addition, Lu et al. and Xie et al. presented that the critical O₂ concentration of oxidation combustion at low temperature is around 5–10% [21, 22]; furthermore,

FIGURE 2: Coal sample in platinum container (≈ 30 mg coal).

TABLE 1: Analysis values of coal (air dried basis).

Proximate analysis	Weight (%)
Ash	12.70
Moisture	2.42
Fixed carbon	54.49
Volatile matter	30.39

high temperature combustion with low oxygen concentration ($\leq 5\%$) is regarded as a new generation of high temperature air combustion technology [23]. In other words, even if O_2 is controlled as very low concentration ($\leq 5\%$) in the flow provided to coal sample, accumulated O_2 gas amount is mostly enough to complete oxidation combustion during the heating process. Consequently, CO_2 -rich atmosphere in the experiment was controlled by changing O_2 concentration from 0 to 5%. After that, the flue gas generated from the heated coal, such as CO, CO_2 , O_2 , and HCs, were analyzed in the combustion and gasification process.

The weight reduction ratio after the measurements, x (%), of coal samples was measured against $O_2\%$ with increasing temperature in the atmospheric pressure. In addition, same experiments and flue gas analyses were conducted for pulverized char samples in the CO_2 -rich atmosphere to compare with the measurement results of coal samples.

2. Analytical Approach and Experimental Conditions

2.1. Coal and Char Samples. Coal samples, used for the experiments, were taken from the 8103 face of Tashan colliery in Shanxi province, China. The properties of which were summarized in Table 1. The samples were crushed into particles 0.25 to 0.5 mm in diameter and dried in a vacuum desiccator. The volume of crushed coal particles was less than that of the platinum container placed in TG-DTA which is almost equal to 49.1 mm^3 as shown in Figure 2.

Sample weight placed was about 30 mg, and its porosity was evaluated as 37%. In order to compare coal and char, char samples were made from the same coal samples by heating for 7 minutes in a sealing volatile matter crucible at the temperature of $(900 \pm 10)^\circ\text{C}$ based on ISO 562:1998 for hard coal and coke determination of the volatile matter. In the same manner, the char particles placed in the container were adjusted into the same diameter range of coal.

2.2. Reaction Mechanism. As reported by Luo and Zhou [24] and Huang et al. [25], the processes of coal combustion and gasification are expressed by the following reactions.

(a) Combustion Reaction:

(b) Gasification Reaction:

Reaction equations (1) and (2) are exothermic processes, and reaction equations (3) to (5) are endothermic processes. Carbon in char matrix reacts with oxygen to form CO and CO_2 . However, it still has not been unified which of them is the favoured product. In general, the proportion of CO/ CO_2 in products increases gradually with increasing temperature. Thus, CO is the main product when the reaction temperature is over around 1030°C and other parameters are constant [26].

2.3. Experimental Apparatus and Procedure. The thermal analysis system from 20 to 1400°C in temperature (TG-DTA) used for the present experiments is shown in Figure 3. The thermogravimetric (TG) analyzes sample mass under changing temperature or elapsed time at a temperature program. Differential thermal analysis (DTA) measures the temperature difference between the analyzed sample and a reference material (a substance with no thermal effect in the measured temperature range, such as Al_2O_3 , as shown in Figure 3(b)) at a sample temperature. TG curves of samples reflect the relationship between changes in the sample mass, temperature, and ambient gas. Injected gas species, gas flow rate, and heating rate are shown in Table 2. The flue gas generated from the heated coal, such as CO, CO_2 , O_2 , and HCs, were analyzed by an emission gas analytical system and a gas chromatography system in the combustion and gasification process.

2.4. Definition of Weight Loss Ratio on TG Curves. Thermogravimetric analysis is an established method to study coal oxidation reactions. Based on the fundamental principle of chemical dynamics, we set the reaction model as $f(x)$, in which x is the reaction conversion rate of coal weight loss:

$$x = \frac{m - m_0}{m_0}, \quad (6)$$

where m_0 is the initial sample mass in mg and m is the sample mass in mg at elapsed time t in min.

The TG output showing the ratio of coal sample to reference material (Al_2O_3) needs to be adjusted before commencement of TG-DTA experiments. The empty weight

(a) Photo of experimental apparatus by using TG-DTA

(b) Sketch map of TG heating vessel

FIGURE 3: Schematic diagram of experimental apparatus.

TABLE 2: Experimental conditions of temperatures and gas flow rates for the TG-DTA analysis.

Sample	Gas injected to system	Flow rates (mL min ⁻¹)	Heating rates λ (°C min ⁻¹)
Coal	Air	200	20
	95% CO ₂ + 5% O ₂	100~200	20~40
	96% CO ₂ + 4% O ₂	100	20
	97% CO ₂ + 3% O ₂	100	20
	98% CO ₂ + 2% O ₂	100	20
	99% CO ₂ + 1% O ₂	100	20
Char	100% CO ₂	100~200	20~40
	Air	100	20
	95% CO ₂ + 5% O ₂	100	20
	96% CO ₂ + 4% O ₂	100	20
	97% CO ₂ + 3% O ₂	100	20
	98% CO ₂ + 2% O ₂	100	20
	99% CO ₂ + 1% O ₂	100~200	20~40
	100% CO ₂	100	20

of a platinum cup for the coal sample was calibrated manually to 0 when the output was stable.

Temperature (Θ) was set with a linear gradient against time t in the measurements:

$$\Theta = \Theta_0 + \lambda t, \quad (7)$$

where Θ is the cell temperature in °C, Θ_0 is the initial temperature in °C, and λ is the temperature gradient in °C·min⁻¹.

2.5. Conversion Factor for Heat Generation from DTA Output. At low temperatures less than 200°C, water evaporated from coal sample, and sample mass m reduced from the initial mass m_0 ($m \leq m_0$, i.e., $x \leq 0$) as shown in Figure 4. According to the DTA principle, the DTA voltage output,

Q^* (μV), is proportional to heat generation rate per unit mass, q (J·min⁻¹·mg⁻¹), as the following:

$$q = \beta \frac{Q^*}{m_0}, \quad (8)$$

where β is a conversion factor from μV to J·min⁻¹. Heat of the Datong coal combustion was previously measured as $H = 30300 \text{ kJ} \cdot \text{kg}^{-1} = 30.3 \text{ J} \cdot \text{mg}^{-1}$. Since the DTA curve reached a constant value after 40 min heating, heat of coal combustion was expressed by integrated DTA output from 0 to 40 min using the following:

$$H = \int_0^{\infty} q(t) dt = \frac{\beta}{m_0} \int_0^{40} Q^*(t) dt = \frac{\beta}{m_0} \sum_{i=0}^{40} Q_i^* \cdot \Delta t, \quad (9)$$

where Δt (=1 min in present experiments) is interval time of the DTA output. The relationship between cumulative heat from time 0 to t , and t is shown in Figure 4 with TG curve (x - t). The conversion factor was calculated as $\beta = 0.17 \text{ J} \cdot \text{min}^{-1} \cdot \mu V^{-1}$ from the value of H at 40 min.

3. TG-DTA Analyses of Coal Combustion and Gasification

3.1. Effects of O₂ Concentration and Gas Flow Rate on Coal Reaction. In the experiments, the termination temperature was set to 1400°C with a temperature gradient of $\lambda = 20^\circ \text{C} \cdot \text{min}^{-1}$ in order to reduce the unburned carbon content. The injected gas species, gas flow rate, and heating rate are shown in Table 2.

According to the coal TG curves by injecting air (see Figure 5), the processes of pyrolysis, combustion, and gasification of coal in flow air can be divided into three temperature stages (temperature value is coal body temperature):

- (1) 25 to 108°C: calefactive-evaporated-alleviative process;
- (2) 108 to 276°C: calefactive-adsorption-weight incremental process (O₂ absorption);

FIGURE 4: A typical TG-DTA curve of coal combustion in air (Air flow: 200 mL·min⁻¹; max. temperature: 1000°C; heating rate: 20°C·min⁻¹).

FIGURE 5: TG curves of different gas flow rates and O₂ concentrations in flow gas.

- (3) Over 276°C: calefactive-oxidation and combustion-alleviative process [27].

However, the processes of coal in the CO₂-rich atmosphere can be divided into four temperature stages:

- (1) 25 to 108°C: calefactive-evaporated-alleviative process;
- (2) 108 to 276°C: calefactive-adsorption-weight incremental process (CO₂ absorption);
- (3) 276 to 650°C: calefactive-devolatilization-alleviative process (refer to volatile matter);
- (4) Over 650°C: calefactive-char formation and gasification-alleviative process.

TG results in the CO₂-rich atmosphere with different gas flow rates and O₂ concentrations are shown in Figure 5. When atmospheric temperature is higher than 360°C (at >360°C, the impact of volatile loss on mass is negligible), coal mass reduces with increasing coal body temperature with a

FIGURE 6: DTA curves of different gas flow rates and O₂ concentrations in flow gas.

linear line, especially in air, coal conversion was completed when atmospheric temperature reached 800°C. In the CO₂-rich atmosphere, the coal burning rate for 95% CO₂ + 5% O₂ gas mixture is faster, and its conversion time is shorter than that of injected 100% CO₂ gas. On the other hand, for the case of 95% CO₂ + 5% O₂, the coal burning rate increases by increasing gas flow rate from 100 mL·min⁻¹ to 200 mL·min⁻¹, because provided O₂ amount increases in unit of time and its reaction time decreases. These phenomenons suggest that O₂ amount is the main working factor for coal conversion rate under the same condition. However, for the case of 100% CO₂, the coal burning rate decreases by increasing gas flow rate from 100 mL·min⁻¹ to 200 mL·min⁻¹ when atmospheric temperature is lower than 1100°C. It can be assumed that increasing CO₂ gas flow rate (amount in unit of time) makes the flame propagation speed and the flame stability decline. However, when atmospheric temperature reached 1100°C, the effects of gas flow rate on coal conversion disappeared, because CO₂ gas participated in coal gasification reactions. The phenomenon suggests that CO₂ gas substitutes the role of O₂ gas to improve and stimulate coal conversion in the higher temperature range from 1100 to 1400°C.

As shown in Figure 6, the heat generation rate of coal is the highest by providing air flow. This is due to coal oxidation and combustion being an exothermic process; on the contrary, the reaction between coal and CO₂ is an endothermic process (refer to Section 2.2). Moreover, flame stability and coal temperature in CO₂ gas-rich flow are lower than those in air flow environment. Additionally, when vessel temperature is lower than 1300°C, the heat generation rate of coal in flow gas of 95% CO₂ + 5% O₂ is larger than that of 100% CO₂. However, the one of a larger flow rate (200 mL·min⁻¹) of 100% CO₂ gas got the highest heat generation after the temperature reached 1300°C (see Figure 6). In other words, even if 100% CO₂ gas was provided, the heat was generated by complex gasification reactions between coal and CO₂ gas including a small amount of H₂O in the high-temperature range. In addition, a dip and a peak come out on the DTA curve of the 100% CO₂ gas. The minimum point of the dip appears

FIGURE 7: TG curves of coal under different temperature gradients.

at around 1160°C, and the maximum point of the peak comes forth at around 1300°C. The trough may reflect the known phenomenon that gasification absorbs heat and generates a differential thermal drop. In other words, char residues generated from coal are further converted by the gasification reaction over 1100°C. It can be assumed that coal gasification with CO₂ gas mainly occurs in higher temperature range from 1100 to 1400°C. In addition, present results show that the chemical reaction of coal in the 100% CO₂ differs from air or gas flow containing O₂ over 5%. Those results suggest that the flame propagation speed, the flame stability, and the reaction between unburned carbon and gas have been improved in the high-temperature range.

3.2. Effect of Temperature Gradient on Coal Reaction. In the measurements, the terminal (or maximum) temperature was set to 1400°C with the temperature gradient of $\lambda = 30^\circ\text{C}\cdot\text{min}^{-1}$ or $40^\circ\text{C}\cdot\text{min}^{-1}$ and gas flow rate of 100 mL·min⁻¹ or 50 mL·min⁻¹, and TG-DTA measurement results in the CO₂-rich atmosphere with different gas flow rates are shown in Figures 7 and 8. Comparing the results of coal weight reduction with the previous results shown in Figure 5, the coal weight reduction ratio is not sensitive to the temperature gradient, because it is mainly affected by O₂ concentration and the terminal temperature. However, coal conversion time shortens, and differential thermal peak takes place in advance, and heat generation values increases with increasing temperature gradient from $20^\circ\text{C}\cdot\text{min}^{-1}$ to $40^\circ\text{C}\cdot\text{min}^{-1}$. Especially for the case of 95% CO₂ + 5% O₂, as shown in Figures 6 and 8, the troughs of the DTA curves with temperature gradients of $20^\circ\text{C}\cdot\text{min}^{-1}$ and $30^\circ\text{C}\cdot\text{min}^{-1}$ are unobvious in higher temperature range; however, the trough and the peak of $40^\circ\text{C}\cdot\text{min}^{-1}$ are very evident. The phenomenon suggests that even if 95% CO₂ + 5% O₂ gas was provided, the intensity of gasification reaction instead

FIGURE 8: DTA curves of coal under different temperature gradients.

of oxidation combustion was enhanced by increasing temperature gradient from $40^\circ\text{C}\cdot\text{min}^{-1}$.

In addition, heat generating rates of coal by injecting 95% CO₂ + 5% O₂ ($q = 0.97 \text{ J}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$) and 100% CO₂ ($q = 0.66 \text{ J}\cdot\text{min}^{-1}\cdot\text{mg}^{-1}$) are increased around 50% with increasing temperature gradient from $20^\circ\text{C}\cdot\text{min}^{-1}$ to $30^\circ\text{C}\cdot\text{min}^{-1}$. Furthermore, the heat generation for 95% CO₂ + 5% O₂ with temperature gradient of $30^\circ\text{C}\cdot\text{min}^{-1}$ is higher than those of others. The value of coal heat generation decreases with increasing temperature gradient from $30^\circ\text{C}\cdot\text{min}^{-1}$ to $40^\circ\text{C}\cdot\text{min}^{-1}$ due to endothermic gasification process. In the high-temperature range, the coal conversion is mainly implemented by coal gasification instead of coal combustion, and the temperature gradient is an essential parameter for improving and stimulating coal gasification reactions.

3.3. Effects of O₂ Concentration on Residual and Differential Thermal. Based on TG-DTA results described, the differences of the effects of 100% CO₂ and 95% CO₂ + 5% O₂ gas flow on weight reduction ratio, x , and differential thermal of coal and reaction products are relatively prominent. Therefore, to further investigate temperature range of coal gasification and the effect of O₂ concentration on coal gasification, the TG-DTA measurements of the coal were carried out by setting different termination temperatures of 1000°C, 1200°C, and 1400°C with injected gases of 0 (100% CO₂) to 5% in O₂ concentration, $\lambda = 20^\circ\text{C}\cdot\text{min}^{-1}$, and gas flow rate of 100 mL·min⁻¹. The detailed contents are shown in Table 2.

The TG-DTA results indicate that O₂%, 0 to 5%, contained in CO₂-rich gas flow has relatively strong effect on coal conversion, heat generation, and reaction products for the different termination temperatures as shown in Figures 9, 10, and 11. Coal weight reduction ratio increases with increasing O₂ concentration in the CO₂-rich atmosphere under the same conditions; moreover, heat generation reduces with increasing CO₂ concentration due to intensifying

FIGURE 9: TG-DTA curves of different O_2 concentrations with a temperature of 1000°C . FIGURE 10: TG-DTA curves of different O_2 concentrations with a temperature of 1200°C .

endothermic gasification reaction between coal and CO_2 gas. Especially, it is clear from the DTA curves that the gasification reaction of coal with CO_2 gas mainly occurs in temperature range from 1100 to 1300°C . In addition, the DTA curves in Figures 10(b) and 11(b) indicate that the greater the atmospheric CO_2 %, the larger trough radian of curves in higher temperature range, that is, intension of gasification reaction. The phenomenon suggests that coal conversion to gases will no longer depend on O_2 % in the high-temperature range due to gasification reactions.

Residual or ash that remained in the container was analyzed by an Energy Dispersive Spectrum (EDS) analyzer after TG-DTA experiments. The photos and EDS images of residuals or ashes for different CO_2 concentrations are shown in Figures 12, 13, and 14. The results of carbon molecular ratios, C%, were investigated by EDS analyzer as shown in Figure 15.

The analytic results indicated that carbon molecular ratios at 1000°C before gasification and 1400°C after gasification do not show strong dependency on O_2 %. On the other hand, the trend of C% against temperature shows that the greater was the atmospheric O_2 %, the less residual value of C% was measured in the gasification stage with the termination temperature of 1200°C . In particular, carbon molecular ratios of 4% and 5% O_2 contained in CO_2 -rich gas flow are essentially coincident with those of the termination temperature of 1400°C ; moreover, carbon molecular ratio is nearly constant with gas flow containing O_2 over 4%; in other words, 4% O_2 contained in O_2/CO_2 gas flow reaches to the saturation ratio of coal combustion and gasification reaction in high-temperature range. It can be verified from the EDS images of residuals or ashes at terminal temperature of 1200°C that coal particle surfaces generated many pores in the 100% CO_2 gas flow due to coal gasification with CO_2 .

FIGURE 11: TG-DTA curves of different O₂ concentrations with a temperature of 1400°C.

(a) Photos of residuals

(b) EDS images of residuals or ashes

FIGURE 12: Photos of residuals at various CO₂ concentrations with a temperature of 1400°C.

gas. On the other hand, the difference of carbon molecular ratio with the terminal temperature of 1200°C is large from 0 to 3% O₂. It can be assumed that coal combustion to gases is not sufficient with reaction (2) instead of (1) after the temperature reached 1100°C; furthermore, O₂ amount in unit of time is insufficient for coal conversion within limited heating time. On the other hand, the heat provided by the terminal temperature of 1200°C is not enough to complete

(a) photos of residuals

(b) EDS images of residuals or ashes

FIGURE 13: Photos of residuals at various CO₂ concentrations with a temperature of 1200°C.

coal gasification with CO₂ gas. Therefore, O₂ concentration is the key factor for coal conversion to gases with the terminal temperature of 1200°C. However, for the case of terminal temperature of 1400°C, coal conversion to gases is completed; it is clear from the photos that residuals form molten state as shown in Figure 12(a), because the melting point of coal ash is around 1250°C. In addition, as shown in Figure 11, the value of TG-DTA curve with 95% CO₂ + 5% O₂ gas flow was constant

FIGURE 14: Photos of residuals at various CO₂ concentrations with a temperature of 1000°C.

FIGURE 15: EDS analysis of residual carbon molecular ratios against O₂% in CO₂-rich gas flow.

after the temperature reached 1200°C; however, the ones of 0 and 3% O₂ contained in CO₂-rich gas flow came to constant when the temperature reached 1300°C. Consequently, coal conversion to gases may break away from O₂ gas and promote CO₂ reduction reactions when atmospheric temperature is over 1300°C.

3.4. Coal Weight Loss Rate versus Temperature. As shown in Figure 16(a), the relationship between coal weight loss rate

(equal to conversion rate of coal to gasses) and temperature can be expressed by the following Arrhenius formula:

$$\frac{\Delta V_m}{\Delta t} = A_0 \cdot \exp\left(-\frac{E}{RT}\right), \quad (10)$$

$$\Delta V_m = \frac{m_0 - m}{m_0},$$

where, $\Delta V_m/\Delta t$ is the average rate of coal weight loss at unit time in s⁻¹, m_0 is the initial coal mass in mg, m is the coal mass at elapsed time Δt , in mg, R (=8.314 J·K⁻¹) is the gas constant, T (K) is the absolute temperature, A_0 (s⁻¹) is the pre-exponential factor, and E (kJ·mol⁻¹) is the activation energy.

The measurement results indicate that pre-exponential factor is almost constant; however, activation energy is mainly dependency of O₂ concentration as shown in Figure 16(b); moreover, it decreased gradually with increasing O₂ concentration. Consequently, the Arrhenius equation can be expressed as the following:

$$\frac{\Delta V_m}{\Delta t} = 0.00045 \cdot \exp\left(-\frac{-0.96Y_{O_2,S} + 135.93}{RT}\right), \quad (11)$$

where $Y_{O_2,S}$ is the O₂ concentration at surface of coal particle, in mole fraction.

3.5. Coal Conversion and Heat Generation Rates. Pyrolysis, combustion, and gasification of coal can be clarified from three peaks generated by analyzing time differential values of coal mass denoted by

$$\frac{dx}{dt} = \frac{d[(m - m_0)/m_0]}{dt}. \quad (12)$$

As shown in Figure 17, the range of 20 to 230°C is dominated by evaporation processes. The value of dx/dt decreases gradually at temperature range from 230 to 360°C and becomes near to zero. The process corresponds to gas adsorption onto coal internal surface pores after releasing moisture. Volatile matter and HCs gases separate out from coal matrix in 360 to 650°C and the porous chars form in 650 to 900°C. In the temperature range of 900 to 1400°C, the dx/dt shows large values due to gasification and combustion reactions of chars in the CO₂ rich gas flow containing a small percentage of O₂.

Heat generation rates in unit of coal mass against time t or vessel temperature, denoted by $s = q/dx/dt$ (J·mg⁻¹), are shown in Figure 18. Heat generation rate of coal can be classified into four stages based on changes with temperature.

- (1) 20 to 230°C: coal drying by water evaporation.
- (2) 230 to 360°C: O₂ and CO₂ gases adsorption before oxidation and combustion. The value of s jumps dramatically since its mass change is small against heat generation.
- (3) 360 to 1100°C: coal oxidation and combustion. Maximum peaks of heat generation rate in unit of coal mass are observed, but the value of s reduces gradually with the formation of porous chars.

(a) Arrhenius plots of coal weight loss rate versus T^{-1} (b) The effects of O_2 concentration on A_0 and E FIGURE 16: Coal weight loss rates with different temperatures and O_2 concentrations.

FIGURE 17: Coal conversion rate versus atmospheric temperature.

FIGURE 18: Heat generation rate versus atmospheric temperature.

- (4) 1100 to 1300°C: coal gasification with the reaction between residual carbon and CO_2 gas.

4. Comparisons of Coal and Char

In view of coal properties of oxidation, combustion, and gasification in the CO_2 -rich atmosphere, comparisons of TG-DTA results of coal and char were also conducted by providing the CO_2 -rich gas flow. The contents of experimental temperature and ambient gas are shown in Table 2. In addition, during the experiments, flue gases generated from the heated coal or char particles were simultaneously analyzed by the gas analytical system transferred from TG-DTA using an air pump ($100 \text{ mL} \cdot \text{min}^{-1}$) in order to discuss the optimum $O_2\%$ in the CO_2 -rich gas for coal or char combustion and gasification. Gases of O_2 , HCs, and CO in the CO_2 -rich gas were measured with a time interval of 1 second by the gas analytical system.

4.1. Comparisons of TG-DTA Curves. In the TG-DTA measurements, the termination temperature was set to 1400°C with a temperature gradient of $\lambda = 20^\circ\text{C} \cdot \text{min}^{-1}$, and ambient gas was supplied by 100% CO_2 or 95% $CO_2 + 5\% O_2$ gas with gas flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$. Sample mass used in the experiments was around 30 mg (see Figure 2).

The TG-DTA measurement results of coal and char in the CO_2 -rich gas flow are shown in Figures 19 and 20. Difference of conversion rate between coal and char is obvious with water and volatile matter evaporations in the initial stage of 20 to 230°C as shown in Figure 19. The water and volatile matter separate out from coal particles, but there is no change for char during the period. After that, the stage transfers to the next common stage of forming porous matrix. Coal or char gasification stage is verified at 1100°C by char mass loss in 100% CO_2 atmosphere (see Figure 19). In addition, heat generation rate of char in 95% $CO_2 + 5\% O_2$ gas flow is higher than those in other gas flows as shown in Figure 20. It can be assumed that 5% O_2 in the CO_2 -rich gas flow was

FIGURE 19: TG comparisons of coal and char in the CO_2 -rich atmosphere.

FIGURE 20: DTA comparisons of coal and char in the CO_2 -rich atmosphere.

sufficient to complete char combustion. On the other hand, heat generation of char gasification in 100% CO_2 gas flow is larger than that of coal; the measurement result suggests that the heat of adsorption with char gasification in the gas flow is smaller than that of coal, because of heat consumption from evaporation of volatile matter in coal and the formation of porous chars.

4.2. Gas Generation from Coal or Char by Various O_2 Concentrations. In the TG-DTA heating process, the flue gases generated from the heated coal, such as CO and HCs gases, have been analyzed by the emission gas analytical system. HCs gas amount generated from coal was measured by providing gas flow with various $\text{O}_2\%$. As shown in Figure 21, the gases were generated from coal samples in the temperature range from 400 to 650°C. In the case of char, there is no HCs gas generation in the same condition. It can be determined that HCs gas is formed with the moisture or volatile matter of coal. In addition, HCs generation rate in air is lower than those of other gases; furthermore, HCs generation from coal

FIGURE 21: HCs gas generation from coal in air and CO_2 -rich gas flows.

in 100% CO_2 is evaluated as roughly $1.2 \text{ mL} \cdot \text{g}^{-1}$ -coal that is higher than those of other gases containing O_2 . In other words, under the same condition, low $\text{O}_2\%$ can promote HCs generation in the CO_2 -rich gas flow.

Figures 22 and 23 show CO gas generation from the heated coal or char in air or CO_2 -rich gas flow. In the case of coal in air flow, CO gas concentration is less than 500 ppm at temperature lower than 700°C. On the other hand, CO gas generation from coal in 100% CO_2 gas flow at temperature over 900°C is roughly $235 \text{ mL} \cdot \text{g}^{-1}$ -coal that is the largest among the CO_2 -rich gas flows, although the maximum peak concentration is recorded in 99% $\text{CO}_2 + 1\%$ O_2 gas flow. Moreover, the peak time of CO concentration matches the trough bottom of DTA heat generation curves (refer to Figures 18 and 20) which correctly verifies endothermic processes of coal gasification. It is intuitively confirmed by CO generation area with increasing temperature from 900 to 1400°C as shown in Figure 22.

Additionally, CO generation amount of coal gradually decreases with increasing O_2 concentration from 0 to 5% in the CO_2 -rich gas. Furthermore, CO generation concentrations from coal for 4% and 5% O_2 contained in CO_2 -rich gas flow are almost lower than 300 ppm in TG-DTA heating process which are smaller than that in air flow. The measurement results suggest that the optimum CO_2 -rich gas flow for coal gasification and combustion is evaluated with 96% $\text{CO}_2 + 4\%$ O_2 gas from the present TG-DTA experiments. The analytical result exactly matches the EDS analysis of Section 3.3. Moreover, it can be assumed that CO generation from coal in air partly formed by reaction (2); however, rich CO_2 gas inhibited coal conversion to gases in the temperature range from 20 to 600°C.

On the other hand, CO generation concentrations from char for 2 to 5% O_2 contained in CO_2 -rich gas flow are approximately lower than 300 ppm in TG-DTA heating process. Moreover, nothing but CO gas generation in 99% $\text{CO}_2 + 1\%$ O_2 gas flow is obvious in the CO_2 -rich gas flow. Therefore,

FIGURE 22: CO gas generation of coal in air and CO₂-rich gas flows. FIGURE 23: CO gas generation of char in air and CO₂-rich gas flows.

the optimum CO₂-rich gas flow for char gasification and combustion is evaluated with 98% CO₂ + 2% O₂ gas flow as shown in Figure 23. Similarly, CO generation amount from char samples in 100% CO₂ gas is roughly 460 mL·g⁻¹-char that is also higher than those of other gases. Comparing the results of coal and char samples in 100% CO₂ gas flow, CO gas generation amount of char samples is higher than that of coal samples, because the volatile matter of coal participates in carbon gasification with CO₂ gas and decreases CO gas generation.

4.3. Effects of Temperature Gradient and Flow Rate on Flue Gas Generation. The measurement results of flue gases generated from coal samples in 100% CO₂ gas with different gas flow rates and temperature gradients set to TG-DTA are shown in Figures 24 and 25. In the measurements of coal samples,

FIGURE 24: HCs gas generation of coal with different temperature gradients and gas flow rates.

FIGURE 25: CO gas generation of coal with different temperature gradients and gas flow rates.

the termination temperature was set to 1400°C. Both of CO and HCs gases generations are not sensitive to the gas flow rate because it is mainly controlled by O₂% and temperature range. However, HCs gas generation becomes approximately double by increasing temperature gradient from 20°C·min⁻¹ to 40°C·min⁻¹. Furthermore, CO gas generation amount also increases with increasing temperature gradient, and the peak extent of CO gas concentration is extended against temperature. These measurement results suggest that high temperature gradient accelerates coal gasification and stimulates gasified gases generation. On the contrary, low temperature gradient promotes slow oxidation of coal and gas generation of CO₂.

In the measurements of char samples, the termination temperature was set to 1400°C with a temperature gradient of 20°C·min⁻¹ and 40°C·min⁻¹; ambient gas was supplied by injected 99% CO₂ + 1% O₂ gas with gas flow rate of 50 mL·min⁻¹ and 100 mL·min⁻¹. As shown in Figure 26, CO

FIGURE 26: CO gas generation from char in 99% CO₂ + 1% O₂ gas flow with different temperature gradients and gas flow rates.

FIGURE 27: Comparisons of weight reduction ratio versus temperature gradient between coal and char.

gas generation is not sensitive to gas flow rate; however, the amount of generating CO gas becomes nearly double by increasing temperature gradient from 20°C·min⁻¹ to 40°C·min⁻¹. In addition, one phenomenon occurs in which temperature area of CO gas generated from coal with the temperature gradient of 40°C·min⁻¹ is almost uniform to the area of CO generation by the heated char in the CO₂-rich gas flow under low O₂%. It shows that the condition of high temperature gradient in a CO₂-rich gas flow with low O₂% is beneficial to coal gasification with O₂ incomplete combustion, and CO₂ circulation technology further improves the utilization of CO₂ gas on coal-fired power generation technologies.

4.4. Effects of Temperature Gradients on Coal Weight Reduction Ratio and Gases Generation. As shown in Figure 27, both of weight reduction ratios of coal and char decrease with

FIGURE 28: Cumulative HCs gas versus O₂% for different temperature gradients during 20 to 700°C (0 to 35 min).

FIGURE 29: Cumulative CO gas versus O₂% for different temperature gradients during 20 to 1400°C (0 to 70 min).

increasing temperature gradient at various O₂% in CO₂-rich gas flow. However, coal is more sensitive to the temperature gradient, and its weight decreases more than that of char, since volatile matter of coal participates in converting coal to gases.

In the TG-DTA measurements, the effects of temperature gradient on cumulative HCs and CO gases are shown in Figures 28 and 29. The experimental results indicate that cumulative HCs and CO gases from coal and char are increased by increasing temperature gradient from 20 to 40°C·min⁻¹. Furthermore, the cumulative CO gas volume generated from the char is the largest at temperature gradient of 40°C·min⁻¹. It is clear that the effect of temperature gradient on HCs and CO gases generations decreases with increasing O₂% from 0 to 5% O₂, especially for CO gas. In addition, cumulative CO gas generated from coal in 99% CO₂ + 1% O₂ gas flow with different temperature gradients is essentially coincident with that of char. It can be assumed

that carbon in volatile matter of coal almost converted to CO₂ gas. The measurement results suggest that O₂% is the primary parameter of coal gasification reactions with low temperature gradient. Consequently, the condition of higher temperature gradient and low O₂% less than 1% makes stimulate and enhances generations of gasified gases such HCs and CO.

5. Conclusions

In this study, characteristics of pyrolysis, combustion, and gasification of Datong coal and char were investigated at temperature range from 20 to 1400°C with heating temperature gradient of 20 to 40°C·min⁻¹ in a CO₂-rich gas flow by TG-DTA analyses. The TG-DTA results were discussed to make clear the effects of O₂% in CO₂-rich gas and heating temperature gradient on coal physical and chemical behaviors related to coal gasification with CO₂ and oxygen combustion and underground coal gasification.

The main findings are summarized as follows.

- (1) The processes of coal in CO₂-rich gas atmosphere mainly are divided into two temperature ranges for coal devolatilization, char formation, and gasification.
- (2) Coal mass reduces with increasing coal matrix temperature with a linear line at various O₂ concentrations that is the main impact factor for coal conversion rate at temperature lower than 1100°C. Moreover, coal weight loss against temperature followed the Arrhenius equation.
- (3) There are dip and peak on the DTA curves for 100% CO₂ gas flow. The minimum point of the dip appears at around 1160°C, and the maximum point is at around 1300°C. Coal gasification in 100% CO₂ gas flow is generated mainly in the temperature range from 1100 to 1300°C. Therefore, coal conversion to gases may break away from O₂ gas and promote CO₂ reduction reactions at temperature over 1300°C.
- (4) For the case of terminal temperature of 1200°C, the higher O₂% was in CO₂-rich gas flow, the less C% in was measured in residuals or ashes.
- (5) HCs gas generated from coal was measured at temperature range from 400 to 650°C in the CO₂-rich gas flow, and it can be formed from moisture and volatile matter in coal.
- (6) CO gas generation amount gradually decreases with increasing O₂% during 0 to 5% in CO₂-rich gas flow. Additionally, the peak time on CO gas concentration or generation matched with the time showing the trough bottom of heat generation curves measured by DTA.
- (7) The optimum CO₂-rich gas flow for gasification and combustion reactions of coal and char is evaluated with 96% CO₂ + 4% O₂ and 98% CO₂ + 2% O₂ gas from the present TG-DTA experiments, respectively.
- (8) Temperature gradient per unit time for heating coal and char samples is a secondary essential parameter to improving and stimulating coal and char gasification.

Coal conversion factor is mainly implemented by coal gasification instead of coal combustion when the temperature gradient is over 40°C·min⁻¹.

- (9) The higher temperature gradient accelerates coal and char gasification reaction with CO₂ gas; on the contrary, low temperature gradient promotes coal and char slow oxidation with low gases generation rate.

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