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

Zhigang Li, 1 Xiaoming Zhang, 2 Yuichi Sugai, 1 Jiren Wang, 2 and Kyuro Sasaki 1

1 Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan
2 College of Mining Engineering, Liaoning Technical University, Fuxin 123000, China

Correspondence should be addressed to Zhigang Li; zhiganglee2009@hotmail.com

Received 22 January 2013; Revised 22 April 2013; Accepted 23 April 2013

Academic Editor: Constantine D. Rakopoulos

Copyright © 2013 Zhigang Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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
Postcombustion capture

O₂
Coal/char
N₂

Gasification and combustion (power and heat)

CO₂ and NOₓ

Precombustion capture

O₂
Coal/char
Steam

Gasification or partial oxidation (oxidation)

H₂, CO, CO₂

Postcombustion capture

O₂
Coal/char
N₂

Gasification or partial oxidation (oxidation)

H₂, CO, CO₂

New O₂/CO₂ oxy-fuel combustion capture

O₂
Coal/char
CO₂ and steam

Gasification or partial oxidation (oxidation)

H₂, CO, HCS, CO₂

Coal added steam for enhancing gasification reactions

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,
high temperature combustion with low oxygen concentration (≤5%) is regard as a new generation of high temperature air combustion technology [23]. In other words, even if \( O_2 \) is controlled as very low concentration (≤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 exper-iments, 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 \( (900 \pm 10)^{\circ}C \) 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:

\[
C + O_2 \rightarrow CO_2 
\]  

\[
C + \frac{1}{2} O_2 \rightarrow CO 
\]  

(b) Gasification Reaction:

\[
C + CO_2 \rightarrow 2CO 
\]  

\[
C + H_2O \rightarrow CO + H_2 
\]  

\[
C + 2H_2 \rightarrow CH_4 
\]

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 \( 1030^{\circ}C \) and other parameters are constant [26].

2.3. Experimental Apparatus and Procedure. The thermal analysis system from 20 to 1400\(^{\circ}C\) 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:

\[
x = \frac{m - m_0}{m_0}, \tag{6}
\]

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas injected to system</th>
<th>Flow rates (mL min(^{-1}))</th>
<th>Heating rates (\lambda) ((^\circ)C min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>Air</td>
<td>200</td>
<td>20 and 100 to 200</td>
</tr>
<tr>
<td></td>
<td>95% CO(_2) + 5% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>96% CO(_2) + 4% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>97% CO(_2) + 3% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>98% CO(_2) + 2% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>99% CO(_2) + 1% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>100% CO(_2)</td>
<td>100 to 200</td>
<td>20 and 100 to 400</td>
</tr>
<tr>
<td>Char</td>
<td>Air</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>95% CO(_2) + 5% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>96% CO(_2) + 4% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>97% CO(_2) + 3% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>98% CO(_2) + 2% O(_2)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>99% CO(_2) + 1% O(_2)</td>
<td>100 to 200</td>
<td>20 and 100 to 400</td>
</tr>
<tr>
<td></td>
<td>100% CO(_2)</td>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>

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

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

\[
\Theta = \Theta_0 + \lambda t, \tag{7}
\]

where \(\Theta\) is the cell temperature in \(^\circ\)C, \(\Theta_0\) is the initial temperature in \(^\circ\)C, and \(\lambda\) is the temperature gradient in \(^\circ\)C min\(^{-1}\).

2.5. Conversion Factor for Heat Generation from DTA Output

At low temperatures less than 200\(^\circ\)C, water evaporated from coal sample, and sample mass \(m\) reduced from the initial mass \(m_0\) \((m \leq m_0, \text{i.e., } x \leq 0)\) as shown in Figure 4. According to the DTA principle, the DTA voltage output, \(Q^* (\mu V)\), is proportional to heat generation rate per unit mass, \(q\) (J min\(^{-1}\) \cdot mg\(^{-1}\)), as the following:

\[
q = \beta \frac{Q^*}{m_0}, \tag{8}
\]

where \(\beta\) is a conversion factor from \(\mu V\) to J min\(^{-1}\). Heat of the Datong coal combustion was previously measured as \(H = 30\,300\, \text{kJ kg}^{-1} = 30.3\, \text{J mg}^{-1}\). 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:

\[
H = \int_0^{40} q(t) \, dt = \frac{\beta}{m_0} \int_0^{40} Q^*(t) \, dt = \frac{\beta}{m_0} \sum_{i=0}^{40} Q^*_i \cdot \Delta t, \tag{9}
\]

where \(\Delta t = 1\, \text{min in present experiments}\) 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 \(\beta = 0.17\, \text{J min}^{-1} \cdot \mu V^{-1}\) from the value of \(H\) at 40 min.

3. TG-DTA Analyses of Coal Combustion and Gasification

3.1. Effects of \(O_2\) Concentration and Gas Flow Rate on Coal Reaction. In the experiments, the termination temperature was set to 1400\(^\circ\)C with a temperature gradient of \(\lambda = 20\, \text{C min}^{-1}\) 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\(^\circ\)C: calefactive-evaporated-alleviative process;
(2) 108 to 276\(^\circ\)C: calefactive-adsorption-weight incremental process \((O_2\) absorption);
When atmospheric temperature is higher than 360°C, the impact of volatile loss on mass is negligible, coal mass reduces with increasing coal body temperature with a 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 phenomena 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...
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 $\lambda = 30\ C\cdot \text{min}^{-1}$ or $40\ C\cdot \text{min}^{-1}$ 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 $20\ C\cdot \text{min}^{-1}$ to $40\ C\cdot \text{min}^{-1}$. 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 $20\ C\cdot \text{min}^{-1}$ and $30\ C\cdot \text{min}^{-1}$ are unobvious in higher temperature range; however, the trough and the peak of $40\ C\cdot \text{min}^{-1}$ are very evident. The phenomenon suggests that even if 95% CO2 + 5% O2 gas was provided, the intensity of gasification reaction instead of oxidation combustion was enhanced by increasing temperature gradient from $40\ C\cdot \text{min}^{-1}$.

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 $20\ C\cdot \text{min}^{-1}$ to $30\ C\cdot \text{min}^{-1}$. Furthermore, the heat generation for 95% CO2 + 5% O2 with temperature gradient of $30\ C\cdot \text{min}^{-1}$ is higher than those of others. The value of coal heat generation decreases with increasing temperature gradient from $30\ C\cdot \text{min}^{-1}$ to $40\ C\cdot \text{min}^{-1}$ 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, $\lambda = 20\ C\cdot \text{min}^{-1}$, 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
endothermic gasification reaction between coal and CO₂ gas. Especially, it is clear from the DTA curves that the gasification reaction of coal with CO₂ 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 was the atmospheric O₂ content, the larger trough radian of curves in higher temperature range, that is, intensification of gasification reaction. The phenomenon suggests that coal conversion to gases will no longer depend on O₂ % 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 CO₂ 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 O₂ %. On the other hand, the trend of C% against temperature shows that the greater was the atmospheric O₂ %, 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% O₂ contained in CO₂-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 O₂ over 4%; in other words, 4% O₂ contained in O₂/CO₂ 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% CO₂ gas flow due to coal gasification with CO₂.
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 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 CO$_2$ concentrations with a temperature of 1000°C.

Figure 15: EDS analysis of residual carbon molecular ratios against O$_2$ concentration (%).

Figure 16(a): Photos of residuals
97% CO$_2$
98% CO$_2$
99% CO$_2$
100% CO$_2$

(a) Photos of residuals

95% CO$_2$
96% CO$_2$
97% CO$_2$

(b) EDS images of residuals or ashes

98% CO$_2$
99% CO$_2$
100% CO$_2$

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:

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

(10)

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 $\Delta t$, in mg, $R (=8.314 \text{ J} \cdot \text{K}^{-1})$ 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 O$_2$ concentration as shown in Figure 16(b); moreover, it decreased gradually with increasing O$_2$ concentration. Consequently, the Arrhenius equation can be expressed as the following:

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

(11)

where $Y_{O_2,S}$ is the O$_2$ 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

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

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 CO$_2$ rich gas flow containing a small percentage of O$_2$.

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: O$_2$ and CO$_2$ 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.
(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 mL·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 $\lambda = 20^\circ$C·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 mL·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 evaporation 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...
in 100% CO₂ is evaluated as roughly 1.2 mL·g⁻¹-coal that is higher than those of other gases containing O₂. In other words, under the same condition, low O₂% can promote HCs generation in the CO₂-rich gas flow.

Figures 22 and 23 show CO gas generation from the heated coal or char in air or CO₂-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% CO₂ gas flow at temperature over 900°C is roughly 235 mL·g⁻¹-coal that is the largest among the CO₂-rich gas flows, although the maximum peak concentration is recorded in 99% CO₂ + 1% O₂ 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 O₂ concentration from 0 to 5% in the CO₂-rich gas. Furthermore, CO generation concentrations from coal for 4% and 5% O₂ contained in CO₂-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 CO₂-rich gas flow for coal gasification and combustion is evaluated with 96% CO₂ + 4% O₂ 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 CO₂ 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% O₂ contained in CO₂-rich gas flow are approximately lower than 300 ppm in TG-DTA heating process. Moreover, nothing but CO gas generation in 99% CO₂ + 1% O₂ gas flow is obvious in the CO₂-rich gas flow. Therefore,
the optimum CO\textsubscript{2}-rich gas flow for char gasification and combustion is evaluated with 98% CO\textsubscript{2} + 2% O\textsubscript{2} gas flow as shown in Figure 23. Similarly, CO generation amount from char samples in 100% CO\textsubscript{2} gas is roughly 460 mL.g\textsuperscript{-1}-char that is also higher than those of other gases. Comparing the results of coal and char samples in 100% CO\textsubscript{2} 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 CO\textsubscript{2} 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% CO\textsubscript{2} 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, 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 O\textsubscript{2}% and temperature range. However, HCs gas generation becomes approximately double by increasing temperature gradient from 20°C·min\textsuperscript{-1} to 40°C·min\textsuperscript{-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 CO\textsubscript{2}.

In the measurements of char samples, the termination temperature was set to 1400°C with a temperature gradient of 20°C·min\textsuperscript{-1} and 40°C·min\textsuperscript{-1}; ambient gas was supplied by injected 99% CO\textsubscript{2} + 1% O\textsubscript{2} gas with gas flow rate of 50 mL·min\textsuperscript{-1} and 100 mL·min\textsuperscript{-1}. As shown in Figure 26, CO
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 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...
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.

Acknowledgments
This study was partly supported by the NEDO (P08020) project on Innovative Zero-emission Coal Gasification Power Generation, JSPS KAKENHI Grant-in-Aid for Scientific Research (B) no. 25303030, and the cooperative research project between Kyushu University and Liaoning Technical University on “CO₂ geological storage and utilization for coal.”

References


