

Research Article

Properties and Developments of Combustion and Gasification of Coal and Char in a CO₂-Rich and Recycled Flue Gases Atmosphere by Rapid Heating

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Combustion and gasification properties of pulverized coal and char have been investigated experimentally under the conditions of high temperature gradient of order $200^{\circ}\text{C}\cdot\text{s}^{-1}$ by a CO₂ gas laser beam and CO₂-rich atmospheres with 5% and 10% O₂. The laser heating makes a more ideal experimental condition compared with previous studies with a TG-DTA, because it is able to minimize effects of coal oxidation and combustion by rapid heating process like radiative heat transfer condition. The experimental results indicated that coal weight reduction ratio to gases followed the Arrhenius equation with increasing coal temperature; further which were increased around 5% with adding H₂O in CO₂-rich atmosphere. In addition, coal-water mixtures with different water/coal mass ratio were used in order to investigate roles of water vapor in the process of coal gasification and combustion. Furthermore, char-water mixtures with different water/char mass ratio were also measured in order to discuss the generation ratio of CO/CO₂, and specified that the source of Hydrocarbons is volatile matter from coal. Moreover, it was confirmed that generations of CO and Hydrocarbons gases are mainly dependent on coal temperature and O₂ concentration, and they are stimulated at temperature over 1000°C in the CO₂-rich atmosphere.

1. Introduction

Coal is the most abundant fossil fuel in China. Present recoverable reserves are estimated to be nearly 120 billion tons based on the Key World Energy Statistics 2006 [1], rank third in the world, with potential total reserves far in excess of this amount. Deposits of coal located in most regions in China by the year 2005 will be nearly 1.5 billion tons per year with the bulk being consumed through the combustion processes. Thus, 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. However, nowadays global warming has become prominent; CO₂ emission reduction is of great urgency. According to the Intergovernmental Panel

on Climate Change (IPCC), approximately three-fourths of the increase in atmospheric CO₂ is attributable to burning fossil fuels [2].

According to statistics of the IEA (2007) [3], CO₂ emission from fossil energy consumption in China was accounted for about 19% of the global CO₂ emission, of which coal-fired power plants occupied about 30% of total CO₂ emission in China. Conventional coal fired boilers use air for combustion in which N₂ gas is 79% in volume ratio. It provides only about 15% CO₂ in the flue gas after combustion, thus, the capture of CO₂ from a flue gas for sequestration is not efficient [4, 5]. Furthermore, CO₂ capture cost from the flue gas using amine scrubbing is expected to be relatively high [6]. Consequently, a new zero-emission coal gasification with CO₂ and oxygen combustion technology has been studied for next coal-fired power plants [7, 8], such as the integrated gasification combined cycle (IGCC), including

CO₂ capture and storage (CCS). In this type of plants, recycled flue gas is used to control gasification furnace temperature and make up the volume of the missing N₂ gas to ensure there is enough gas to be combusted and subsequent energy generation via a gas turbine. The basic revenues are the heat gain by hot CO₂ recirculation, syngas cooling, subsequent burning, and steam boiler after gas turbine, and N₂ gas heating is not needed. Consequently, a flue gas consisting mainly CO₂ and water steam is generated; thus CO₂ can be easily separated by steam condensation [9]. In addition, pulverized coal-fired power plants could be the best candidates to install CO₂ capture system, of which oxy-fuel or CO₂/O₂ combustion technology is one of promising methods to evade problems of CO₂ separation [10].

The objective of this study is to investigate coal gasification and combustion processes in the CO₂-rich or oxy-fuel atmosphere instead of air by application of conventional equipment.

Thermo gravimetric differential thermal analyzer (TG-DTA) [11] has been used to provide measurement data for essential parameters of coal pyrolysis, combustion, and gasification; however, it is restricted to temperature gradient of coal samples heated by degree centigrade per minute instead of per second; thus, it usually takes several ten minutes or longer time to get gasification temperature around 1000°C. Even if O₂ is controlled as very low concentration in the flow provided to the coal sample with TG-DTA equipment, the carbon-to-oxygen ratio is mostly enough to complete oxidations during the period of increasing temperature. In other words, the heating time for TG-DTA is extremely longer than that in actual gasification furnaces with strong thermal radiation. Coal oxidation before reaching to a targeted test temperature has unpredictable physical and chemical effects on the reactions in specific gaseous atmosphere [12]. Therefore, it is required to make rapid heating to investigate the coal properties by providing same order of temperature gradient observed in the commercial processes.

In this study, a CO₂ gas laser was used to achieve rapid heating of coal samples with temperature gradient of order 100°C·s⁻¹ to reach targeted temperature of combustion and gasification. In the coal heating experiments under CO₂-rich atmospheres with O₂ concentrations of 5% and 10%, HCs and CO gases were monitored, because they are important gases indicating typical substances generated by combustion and gasification chemical reactions between coal and gases [13]. Liu presented the properties in TGA experiments with a high-volatile UK bituminous coal and an anthracite coal at the heating rate of (2.5~12.5°C·min⁻¹) in 10% O₂/90% CO₂ environment [14]. Weight reduction ratio or conversion ratio of the coal samples was measured against O₂ concentration (%) in the atmosphere after the heating experiments. In addition, coal-water mixtures with different water/coal mass ratio were studied in order to investigate effects of water on coal gasification and combustion. Besides, the differences of measurement results using coal and char were analyzed so as to specify the source of hydrocarbon gases in the chemical reactions.

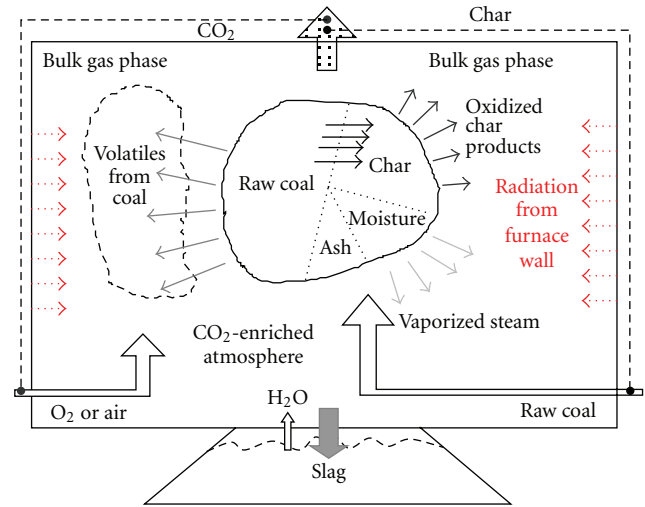
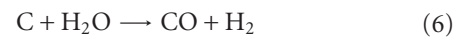
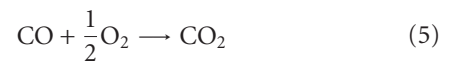
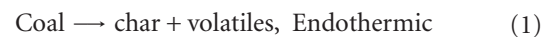


FIGURE 1: Schematic diagram showing reactions in coal gasification furnace [15].

2. Elements of Coal Reactions

Descriptions of coal reaction processes have been tried by a “coal particle reaction” model [15], but any single model cannot exactly expound all reactions for different varieties and sizes of coal. A schematic model of reacting coal particles in a coal gasification furnace is modified as shown in Figure 1. The model suggests that the particle, at any time in the reaction process, is composed of moisture, raw coal, char, and ash (mineral matter), and the coal particle is also surrounded by its volatilized matter with injected CO₂ and O₂ or air.

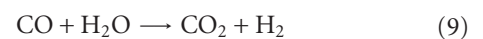
Coal reactions have been divided into two distinct components [16]. One is devolatilization of the raw coal; the other one is oxidation of the residual char. The main reactions which take place in the combustion and gasification processes are the following [17]:



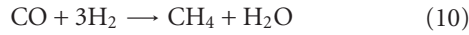
Hydrogenation:



Water shift reaction:



Methanation:



Carbon in char matrix reacts with oxygen to form CO and CO₂. However, it still has not been unified which of them is the main formulated product. In general, the ratio of CO/CO₂ in the gaseous product increases gradually with higher temperature. Further, CO gas is the main reaction product at temperature over around 1030°C [18].

In addition, CO/H₂ ratio is an important parameter that is affected by the water-gas shift reaction when a synthetic fuel gas is used for gas turbine power generation. The gasifier gases also contain some methane (CH₄), because hydrogenation of carbon occurs with hydrogen (H₂) in the fuel gas; moreover, some CH₄ gas can be produced from a reaction between CO and H₂. The methanation reaction increases the calorific value of the gas, but its reaction rate is very low except at high gasification pressure or use of a catalyst. The shift reaction increases amount of H₂ in the gases. These shift and methanation reactions are particularly discussed for the IGCC [17].

In the experiments, CO₂ was injected into the vessel to make CO₂-rich atmosphere before heating the coal sample; thus injected CO₂ and generated CO₂ in the cell were not specified by monitoring CO₂ and measuring CO/CO₂ ratio. Hurt and Mitchell [19] gave an empirical expression:

$$\frac{\text{CO}}{\text{CO}_2} = 3 \times 10^8 \exp\left(-\frac{60000}{RT_p}\right) \quad (11)$$

by neglecting the effects of O₂ concentration and measuring the combustion temperature and combustion rate in a dilute stream of coal particles. Zeng and Fu [20] presented the expression:

$$\frac{\text{CO}}{\text{CO}_2} = 600(\rho Y_{\text{O}_2, \text{s}})^{0.24} \exp\left(-\frac{8000}{T_p}\right) \quad (12)$$

from the oxidation of high-purity graphite by using carbon oxidation mechanism for the formation of CO and CO₂ if O₂ concentration at the carbon surface is known. In this study, it was difficult to determine accurate ratio of CO/CO₂ in the system due to the effects of water shift and methanation reactions. However, it can be estimated from the measurement results of CO concentration and char conversion ratio to gases.

Additionally, the HC gas was monitored in the flue gas, it was not able to distinguish the HC gas generated from the external water (mixing water) or the internal water (adsorbing water) and volatile matter of coal. However, it is able to be evaluated by comparisons between the results of coal water mixture and char water mixture.

3. Experimental Apparatus and Procedure

3.1. Coal and Char Samples. Coal samples were taken from the 8103 face of Tashan colliery in the Shanxi province, China. The coal contents were summarized in Table 1. Coal

TABLE 1: The properties of coal sample.

Item	Coal sample of Datong	
Proximate analysis (wt% dry basis)	Ash	8.20
	Volatile matter	29.4
	Fixed carbon	62.4
	Fuel ratio (= FC·VM ⁻¹)	2.12
	HHV (kJ·kg ⁻¹)	30300
	LHV (kJ·kg ⁻¹)	29300
Ultimate analysis (wt% dry basis)	C	76.9
	H	4.30
	N	0.83
	O	7.20
	S	0.67
	Combustible S	0.62
	Noncombustible S	0.05
Ash fusibility (K, ASTM method in reducing atmosphere)	IDT	1353
	ST	1398
	HT	1403
	FT	1488
Ash fusibility (K, DIN method in oxidizing atmosphere)	EP	1413
	SP	1463
	FP	1753

samples were crushed into particles 0.25 to 0.5 mm in diameter and dried in a vacuum cell. The volume of crushed coal particles used for present experiments was less than 49.1 mm³ which is almost equal to a volume of a ceramic cylindrical container 5 mm in diameter as same as one used for TG-DTA measurements. In addition, compare coal with char, according to ISO 562:1998, hard coal and coke-determination of volatile matter, 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 ± 10)°C. In the same manner for the case of coal, the char samples were dried in the vacuum cell and crushed into particles 0.25 to 0.5 mm in diameter.

Three kinds of coal samples were used for the experiments as shown in Figure 2. The coal-water mixture is a new kind of fuel suitable both for large and industrial power plants due to its technological and economical aspects [21]. The objective of mixing with varying external water is to investigate that the effects of water content on the basis of the same quality of coal sample refer to the reaction mechanisms of water vapor-gas shift and methanation. By contrast, water content in volatile matter (internal) of dried coal sample was controlled by adsorbing water in order to analyze the difference between external water and internal water. For the case of measurements using the dried coal sample (Coal no. 1, Figure 2(a)), 20 mg was used for the measurement. The 2nd sample (Coal no. 2, Figure 2(b)) is the coal-water mixture, which is mixed by 20 mg of dried coal with varying water. The 3rd one is the coal adsorbing water (Coal no. 3,

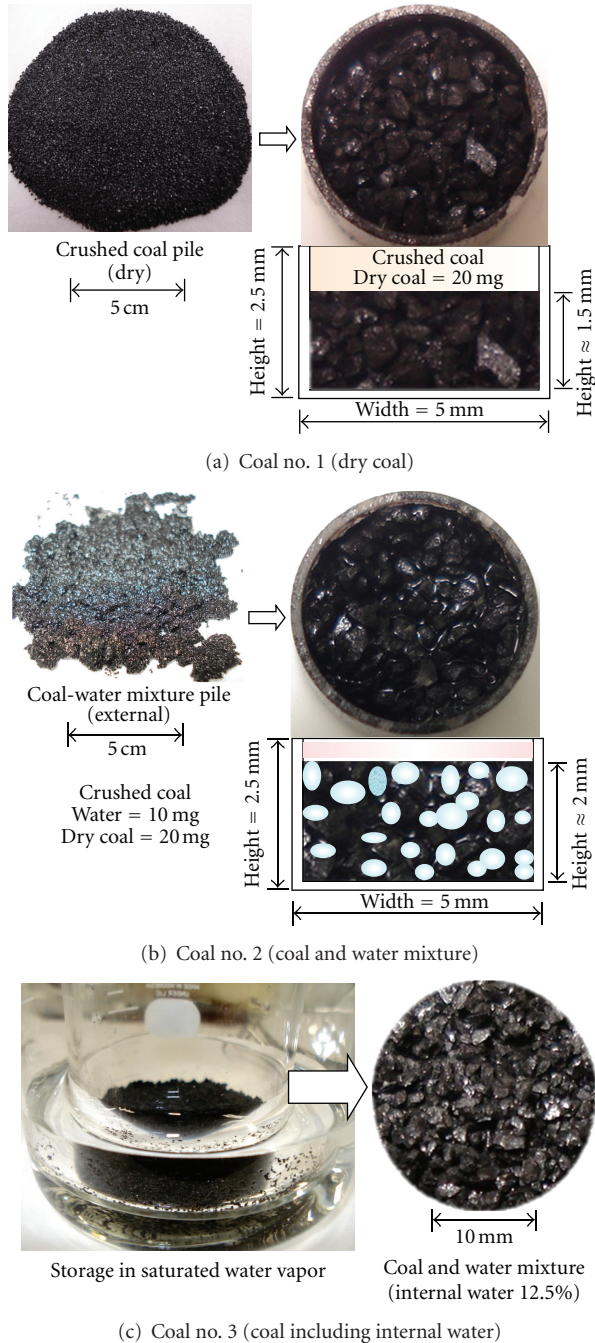


FIGURE 2: Three kinds of coal samples.

Figure 2(c) prepared by dipping 20 mg dry coal particles in water placed in a vacuum cell. The water remained on outer surface of coal particles was removed with a paper, and after that it was kept in a closed atmosphere with saturated water vapor to keep constant water content of the sample during one month. Similarly, three kinds of char samples were used for the experiments as shown in Figure 3. For the case of measurements using dried char sample (Char no. 1, Figure 3(a)), 20 mg was used for the measurement as same as the mass of coal sample. The 2nd sample (Char no. 2,

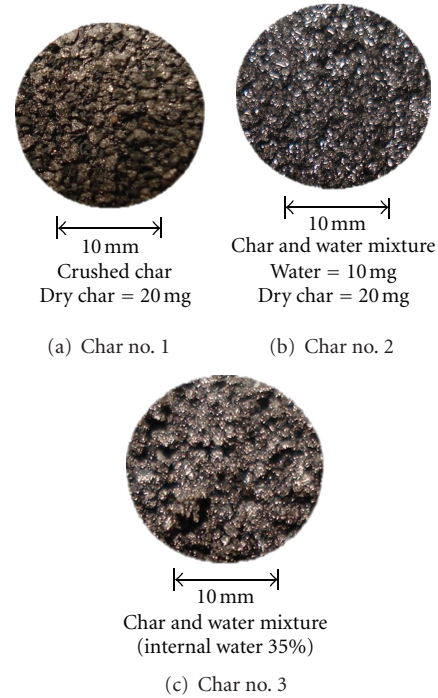


FIGURE 3: Three kinds of char samples.

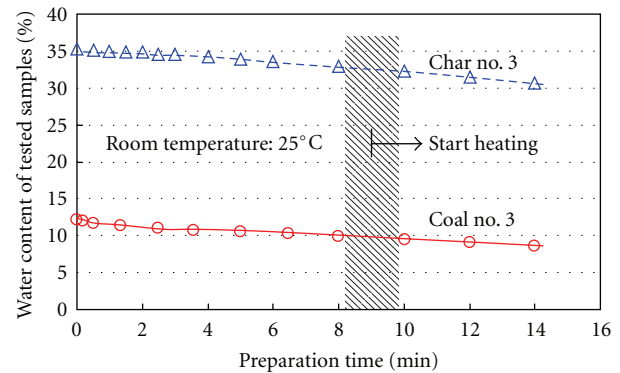


FIGURE 4: Water loss by evaporation from Coal no. 3 and Char no. 3 for preparation time.

Figure 3(b) is char-water mixture, which is mixed by 20 mg of dried char with varying water. The 3rd one is also the char adsorbing water (Char no. 3, Figure 3(c)) prepared by dipping 20 mg dry char particles in water placed in a vacuum cell, in the same way, then it was kept in a closed atmosphere with saturated water vapor.

Figure 4 indicates water content of Coal no. 3 and Char no. 3 became slightly smaller by water evaporation with time elapsing. The water content in samples of Coal no. 3 and Char no. 3 became 10 to 9.5 wt% and 32.7 to 32 wt% against dry coal mass and dry char mass after 8 to 10 minutes, respectively.

3.2. Laser for Heating and Initial Temperature Gradient. Present experimental apparatus is shown in Figure 5. The CO₂ gas laser (Coherent Inc., Model C-20, max. power: 30 W,

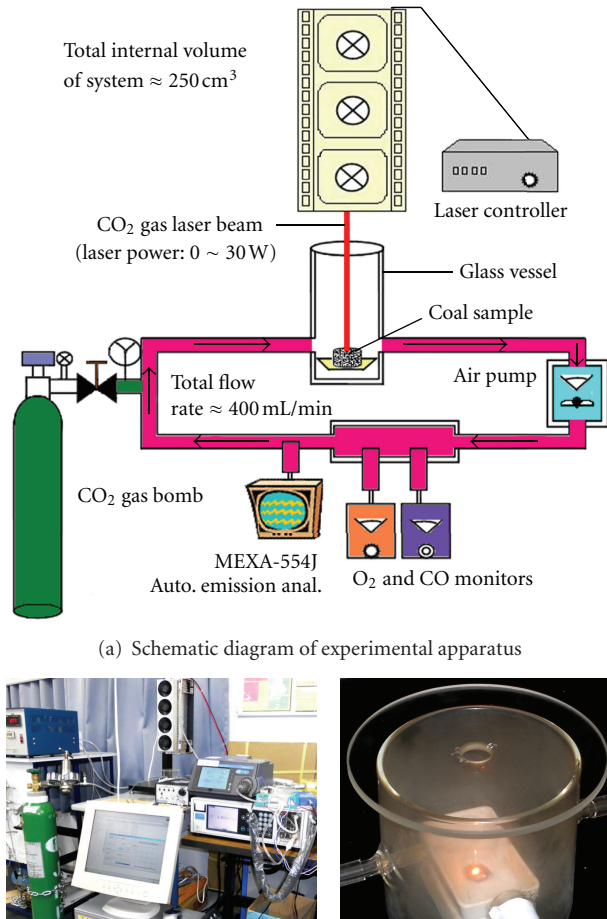


FIGURE 5: Experimental apparatus.

beam diameter: 2 mm) was used to heat up samples of coal and char over the targeted temperature within a short time less than 10 s. The laser power was set up from 1 to 10 W, and the sample temperature ranged from around 100 to 1000°C.

Taking the dried coal samples, rapid heating of coal particles (height ≈ 1.5 mm; see Figure 2(a)) was sustained 2 min, because generating amount of CO gas gradually decreased with coal consumption after 2 min. The typical curves of temperature rise within 2 min after start of heating are shown in Figure 6. The heated coal body temperature was measured by a thermo camera (NEC-SANEI, Model 7102MX) and analyzed with the software (NEC-SANEI, InfReC Analyzer NS9500) under different laser powers. The heating in the experiments was carried out under a constant laser power, P_L (W), and it was turned off after 2 min. In the initial phase (≤ 5 s) of the heating, coal body temperature increased by an initial temperature gradient, after that coal body temperature was indicating approximately constant temperature (see Figure 6). In other words, it merely took 5 s to reach a targeted test temperature for coal gasification and combustion; the laser heating was balancing with radiative heating loss from the sample.

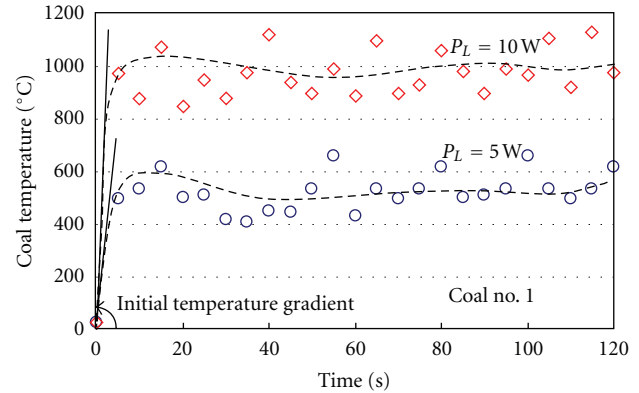


FIGURE 6: Coal sample no. 1: temperature versus time.

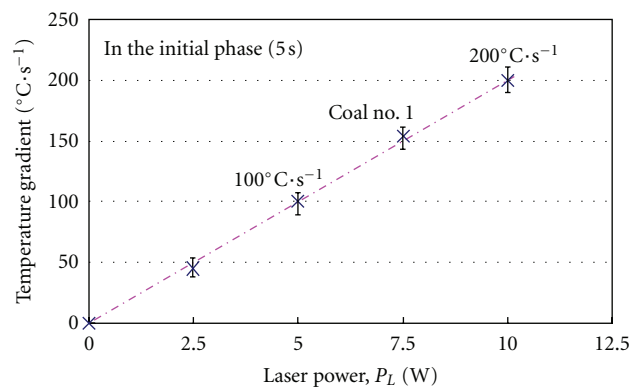


FIGURE 7: Initial coal temperature gradient versus laser power.

Coal temperature and its temperature gradient were mainly dependent on laser power; further the targeted temperature was distinct. The initial temperature gradient was evaluated by changing P_L as shown in Figure 7. For example, the initial temperature gradient is $200^\circ\text{C}\cdot\text{s}^{-1}$ for $P_L = 10$ W.

3.3. Control of Atmosphere in the Vessel. As shown in Figure 5, the experiments were carried out by heating coal or char samples in a glass vessel (approximately 250 mL in volume) filled with CO_2 -rich atmosphere. Firstly, the sample was set in the ceramic container placed on the bottom of the vessel. The vessel was covered by a glass plate with a 10 mm hole in diameter as shown in Figure 5(b), in order to make pass of the laser beam so that the vessel was not completely sealed against the air. Therefore, small amount of air (approximately 21% O_2 , 79% N_2) was retained in the vessel. Secondly, O_2 concentration in the atmosphere was controlled to 5% and 10% by CO_2 gas injection rate (80 and $40\text{ mL}\cdot\text{min}^{-1}$) into the circulated flow on the basis of the O_2 concentration. After that, the atmosphere in the vessel was circulated by two air pumps (total flow rate: $400\text{ mL}\cdot\text{min}^{-1}$) with mixing CO_2 gas provided from a CO_2 gas bomb and circulating flow into the vessel. In general, it took 5 to 10 minutes to make stable CO_2 -rich atmosphere and the specific $\text{O}_2\%$ in the vessel before heating the sample.

TABLE 2: Ambient gas contents.

Gas injected to system	N ₂ (%)	O ₂ (%)	CO ₂ (%)	Flow R. injected (mL·min ⁻¹)
Air injection	79	21		40
CO ₂ injection	no. 1	20	75	80
	no. 2	40	50	40
N ₂ injection	90	10		40

3.4. Monitoring Gases Generated by Rapid Heating Tested Samples in CO₂-Rich Atmosphere. During the rapid heating experiment in CO₂-rich atmospheres with 5% and 10% O₂, plenty of flue gases generated from the heated coal or char particles were simultaneously transferred to the gas monitors by using the two air pumps. Then concentrations of O₂, CO₂, HC and CO gases in the mixture of O₂/CO₂, and recycled flue gases were measured with time interval of 1 second by using CO monitor (Horiba Co., Ltd., Model VA 3001CO), O₂ detector (New Cosmos Co., Ltd., Model XO-326AL), and a gas monitor (Horiba Ltd., Model MEXA-554J). In the initial stage, the ambient gases were measured by using the monitors as shown in Table 2. In the system, flue gases were firstly dedusted and cooled to room temperature condition by using a filter and then recirculated into the vessel, thus CO and HCs gases were mixed and averaged to constant concentrations after turning off the laser. During the rapid heating, the gases from the heated coal and char samples were mixed in the vessel. Generating amount of CO or HCs gas is roughly proportional to each gas concentration in the circulating flow line connected to the vessel 250 mL in volume. In this study, the gas concentration-time curves of CO and HCs were measured and discussed on the chemical reactions among coal or char with O₂, CO₂, and H₂O.

4. Results and Discussions

4.1. Coal Weight Reduction by Rapid Heating in CO₂-Rich Atmosphere. Experiments on coal particles' combustion and gasification by rapid heating were conducted in the ambient gases controlled to air injection, N₂ injection, CO₂ injection no. 1 and no. 2 under the atmospheric pressure. The initial weights of Coal no. 1 samples were 20 mg. Figure 8 shows coal weight reduction ratio of Coal no. 1, x (%), against the laser power. Coal weight reduction increases with increasing coal body temperature with a linear line, in which the one by air injection is comparatively higher than those in CO₂-rich atmosphere. In addition, the coal weight reduction by providing N₂ and 10% O₂ mixture gas has an obvious inflection point when the atmospheric temperature is higher than 400°C (refer to Figure 7); the reason can be assumed that N₂ gas does not make coal conversion, but coal gasification with CO₂ gas promotes coal conversion to gases.

It is expected that recycled flue gas (mainly CO₂) is used to control the flame temperature and make up the volume of the missing N₂ to ensure there is enough gas to carry the heat through the furnace. This may indicate the feasibility of oxy-fuel or CO₂/O₂ combustion technology.

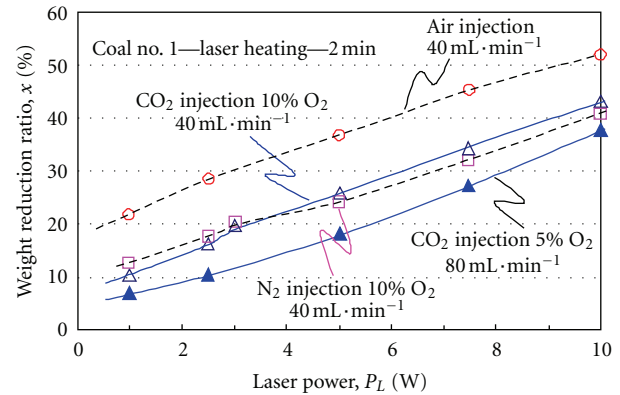


FIGURE 8: Comparison of weight reduction ratio, x (%) with different gases injection.

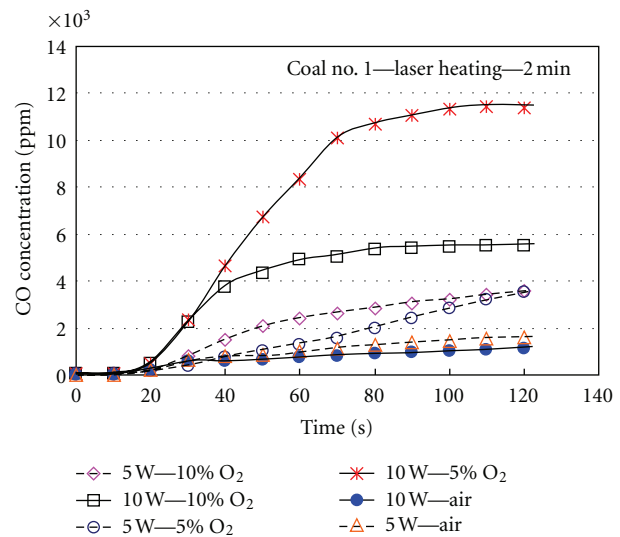
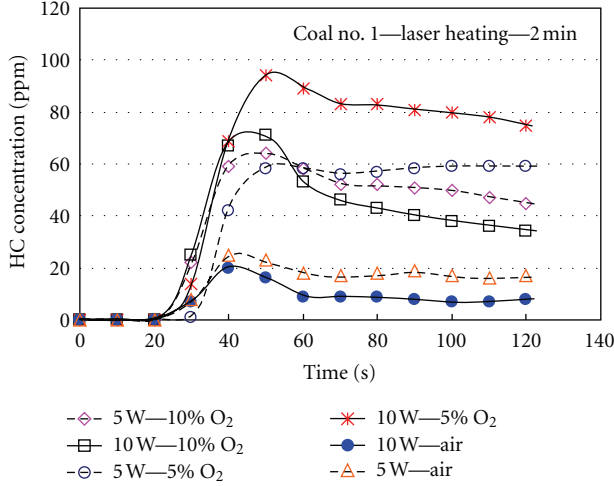


FIGURE 9: CO gas generated in CO₂-rich and air atmospheres.

Figures 9 and 10 show CO concentration and HCs concentration amounts generated with CO₂-rich and air atmospheres, respectively. For the case of CO₂-rich atmosphere, CO and HC gases generated from the heated coal particles increase with higher laser power under the same O₂ concentration due to getting higher temperature. Furthermore, lower O₂ concentration or higher CO₂ concentration is of benefit to generating CO and HC gases. In the case of air injection, lower laser power opportunely promotes to generate CO and HC gases. The measurement results show a phenomenon that carbon elements of high weight reduction ratios with 10% O₂ mainly produce CO₂ compared with 5% O₂, not gasified gases, such as CO and HC gases. That is, not only CO/CO₂ ratio is dependency of high temperature but also CO₂ concentration in coal gasification atmosphere is an operation parameter for CO₂/O₂ combustion technology.

4.2. Coal Weight Loss Rate versus Temperature. As shown in Figure 11(a), the relationship between coal weight loss rate

FIGURE 10: HCs gas generated in CO₂-rich and air atmospheres.

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

$$\frac{dV_m}{dt} = k_0 \cdot \exp\left(-\frac{E}{RT}\right), \quad (13)$$

$$V_m = \frac{m_0 - m_t}{m_0},$$

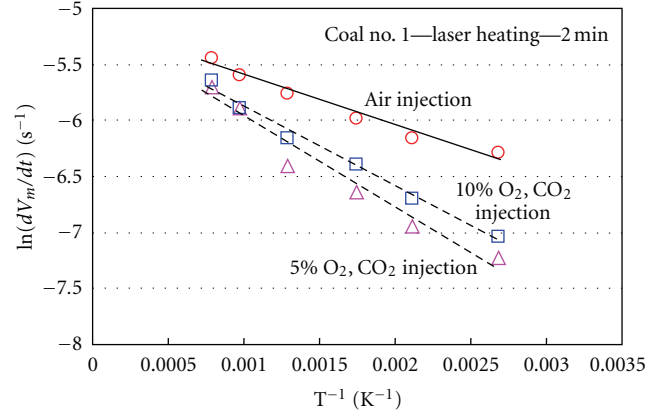
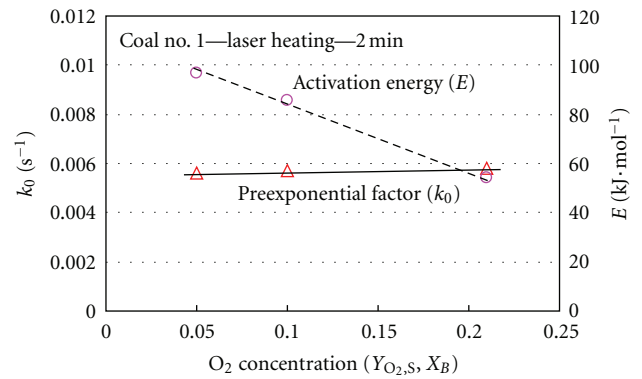
where dV_m/dt is coal weight loss rate at unit time in s^{-1} , m_0 is initial coal mass in mg, and m_t is coal mass at elapsed time t , in mg, k_0 (s^{-1}) is pre-exponential factor, E ($\text{Kj} \cdot \text{mol}^{-1}$) is activation energy, R ($= 8.314 \text{ J} \cdot \text{K}^{-1}$) is gas constant, T (K) is absolute temperature.

The measurement results indicate that preexponential factor is almost constant; however, activation energy is mainly dependency of O₂ concentration as shown in Figure 11(b); moreover, it decreased with increasing O₂ concentration. Consequently, the Arrhenius equation can be expressed as follows:

$$\frac{dV_m}{dt} = 0.0057 \cdot \exp\left(-\frac{-2.7Y_{\text{O}_2,S} + 111.22}{RT}\right), \quad (14)$$

where $Y_{\text{O}_2,S}$ is O₂ concentration at surface of coal particle, in mole fraction, X_B .

4.3. Effect of Water Content on Reactions of Combustion and Gasification of Coal and Char. In view of reactions between coal and gases, especially water-shift reaction (9), coal water mixtures (Coal no. 2) with different water/coal mass ratio were studied in order to further investigate roles of water for coal combustion and gasification characteristics in CO₂-rich atmosphere. In addition, samples of Char no. 1 and no. 2 were also studied in order to discuss the effects of water and volatile matter on the ratio of CO/H₂. In the experiments, the laser power was set up from 2.5 to 10 W; the ambient gases were set up to CO₂ injection no. 1 and no. 2 controlled by injecting rate of CO₂ with monitoring the O₂ concentration; the heating period was 2 minutes. On

(a) Arrhenius plots of coal weight loss rate versus T^{-1} (b) The effects of O₂ concentration on k_0 and E FIGURE 11: Coal weight loss rate with different temperature or O₂ concentration.

the basis of a typical water/coal mass ratio [21], mixing by water 10 mg and dry coal 20 mg, total 30 mg of coal no. 2 was placed in the container. In the same manner, total 30 mg of char no. 2 was used in the measurements. In the heating process, heat for evaporating water of 10 mg is expected as around 25 J which is equal to power generated with 2 W laser during 12.5 s and generates 12.6 mL steam or water vapor in the standard condition.

The expected effects of water on coal oxidation and combustion are cooling the samples by latent heat of water evaporation and promoting chemical reactions between H₂O vapor (steam) and gases generated by rapid heating coal. The measurement results of coal and char weight reduction ratios or coal and char conversion ratios to gases, x (%), were shown in Figure 12.

Comparing with the previous experiments, coal mass loss by mixing water is obviously higher than that of the dried coal sample under the same condition. Moreover, the effect of water content on char conversion ratio is also distinct. These results suggest that a series of chemical reactions enhanced conversions of coal and char to gases with H₂O vapor. In addition, there is little difference between external water and internal water for coal weight reduction ratio, as well as char.

There is a time lag around 10 s between Coal no. 1 and no. 2 during the period of 20 to 40 s for CO and HC gas

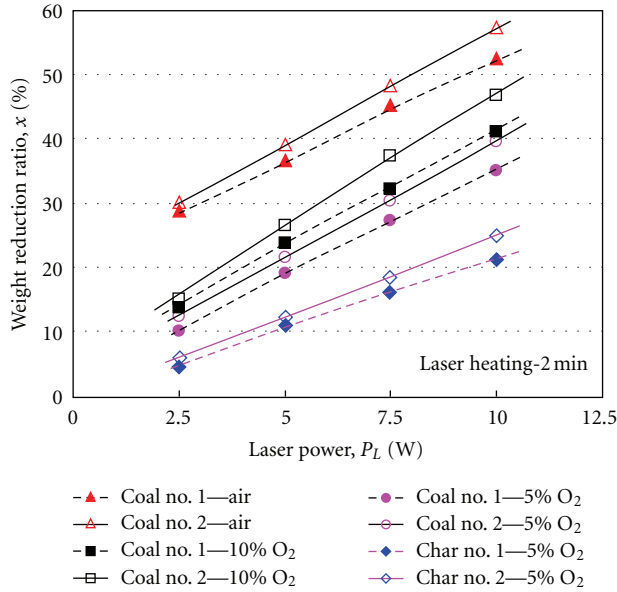


FIGURE 12: Comparisons of weight reduction ratio, x (%) with different samples and gases injection.

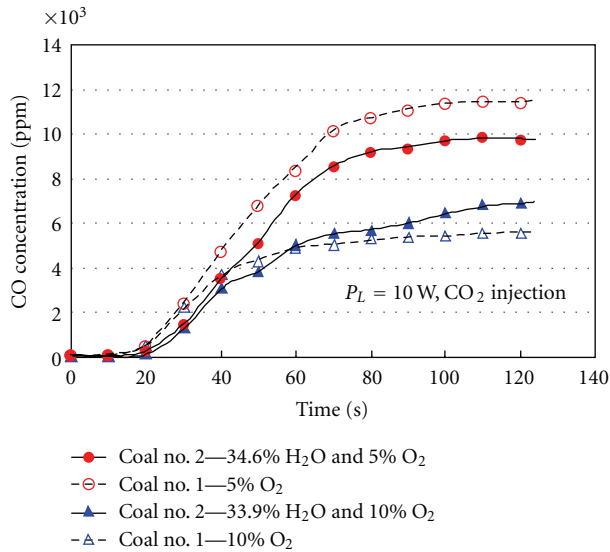


FIGURE 13: Comparisons of coal and coal water mixture on CO gas generation by CO_2 injection.

generations as shown in Figures 13 and 14. It comes from heat consumption for water evaporation, especially in HC gas generation.

In the case of the Coal no. 2 (coal-water mixture), generating amount of CO gas is decreased in the atmosphere of 5% O_2 compared with the Coal no. 1, on the contrary, which is increased with 10% O_2 as shown in Figure 13. In addition, generating amount of HCs gas for Coal no. 2 is comparatively increased under the conditions of 5% and 10% O_2 as shown in Figure 14. Especially, the effect of water on HCs generation with 10% O_2 is more obvious than that of 5% O_2 . It shows a possibility that water-gas shift reaction had

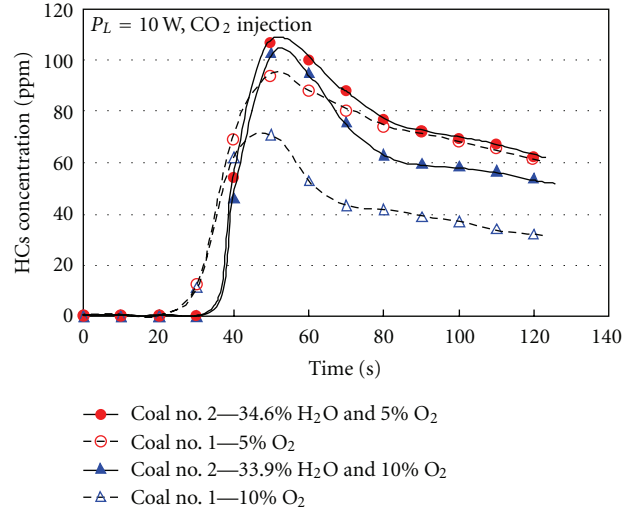


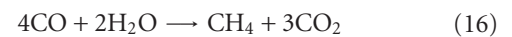
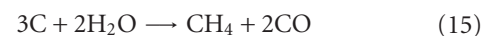
FIGURE 14: Comparisons of coal and coal water mixture on HCs gas generation by CO_2 injection.

TABLE 3: Comparisons of flue gases between Coal no. 1 and Coal no. 2 for laser power of 10 W.

$\text{O}_2\%$	Max. CO (ppm)		Max. HCs (ppm)		HCs/CO (%)	
	no. 1	no. 2	no. 1	no. 2	no. 1	no. 2
5	11431	9826	94	107	0.8	1.1
10	5523	6938	71	103	1.3	1.5

an influence on the ratio of CO/HC. Measurement results of flue gases concentrations are summarized in Table 3.

These experimental results indicate that partial water vapor substitutes the role of O_2 gas to participate in coal gasification when O_2 concentration is 5%, and then which promotes methanation reaction (refer to reaction mechanisms (6) and (8)); thus, partial H_2 serves as the intermediary product during the process. Finally, reaction (6) combines with reaction (8) to form new reaction (15) and promote the hydrogenation of carbon result in the reduction of CO concentration compared with the Coal no. 1. In this case, the reaction ratio of $\text{C}/\text{H}_2\text{O}$ is 3 : 2 as shown in (15). However, when O_2 concentration is 10%, CO takes place a series of chemical reactions with water vapor and H_2 (refer to reaction mechanisms (9) and (10)); therefore, partial H_2 serves as the intermediary product during the process. At last, reaction (9) combines with reaction (10) to form new reaction (16) and further increase HCs concentration. In this case, the reaction ratio of $\text{CO}/\text{H}_2\text{O}$ is 2 : 1 as shown in (16):



After that generating amount of CO gas gradually increases along with the consumption of water vapor. These experimental results suggest that the priority of coal gasifications is $\text{O}_2 > \text{H}_2\text{O} > \text{H}_2$; that is, the priority of reactions is reaction (2) > (6) > (8). In other words, coal gasification with O_2

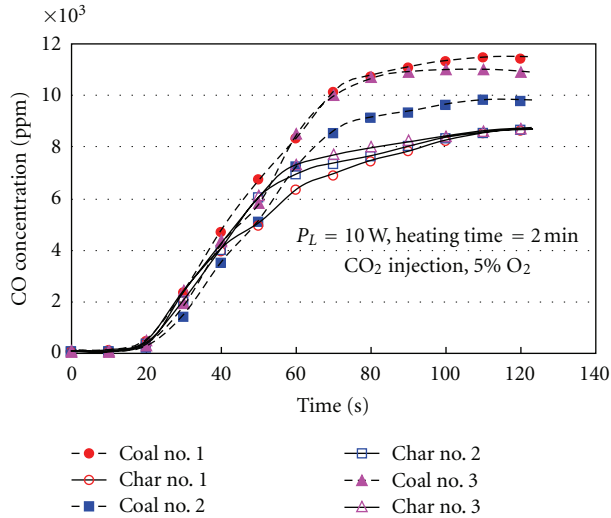


FIGURE 15: Comparison of the six kinds of samples tested for CO gas generation by CO₂ injection.

gas is completed in the 10% O₂ atmosphere, however, which is insufficient in the 5% O₂ atmosphere, because laser rapid heating is partial and instantaneous.

On the basis of above measurements and discussions, the following experiments were conducted with CO₂-rich atmosphere with 5% O₂ (5% O₂, 20% N₂, 75% CO₂) and laser power of 10 W. Figure 15 shows generating amount of CO gas from the samples. These experimental results expect that the mixture of volatile matter and char or water and coal in the furnace as shown in Figure 1 is more beneficial in CO gas generation. In addition, CO gas generations of the three kinds of char samples gradually close to a same value after 100 to 120 s due to the consumption of water vapor. These measurement results can assume that CO gas concentrations generated from the three kinds of coal samples distinguish those of the three kinds of char samples due to the difference of volatile matter. Additionally, in order to confirm the ratio of CO/CO₂ and specify the source of HCs gas, the flue gas compositions of the six kinds of samples tested after the heating were investigated on the basis of reaction mechanisms. In the case of Char no. 1 (dried char), molar weight of carbon was calculated as 0.358 mole by weight reduction ratio of char, molar weight of CO gas was measured as 0.095 mole. Compared with Char no. 1, molar weight of carbon in Coal no. 1 was calculated by fixed carbon ratio of coal mass loss. In the process, molar weight of HCs gas was neglected because generating amount of HCs gas was little. Thus, the CO/CO₂ ratios of coal and char were calculated to 1 : 2.0 (ignoring the influence of water in volatile matter on coal gasification) and 1 : 2.8 in the atmosphere of 5% O₂, respectively. That is, the CO/CO₂ reaction ratio of coal is showing higher 8% than that of char. Furthermore, HCs gas was not detected for Char no. 1 and no. 2; however, HCs gas was detected for Char no. 3 less than 10 ppm during the experiment. The results suggest, CO and H₂ gases are mainly products in gasification furnace for char water mixtures instead of CO and HCs gases when O₂ concentration is 5%. It can be concluded that HCs gases

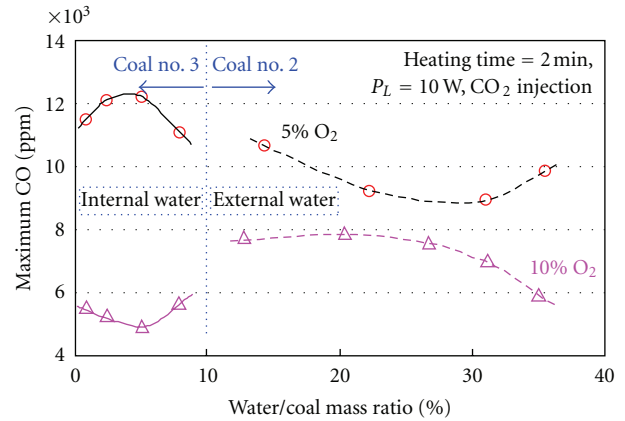


FIGURE 16: Maximum CO gas concentration versus water/coal mass ratio.

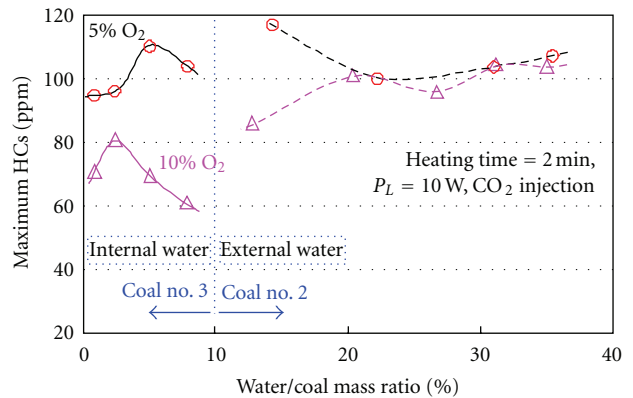


FIGURE 17: Maximum HCs gas concentration versus water/coal mass ratio.

from the coal and coal water mixture in a gasification furnace are mainly generated from volatile matter of coal.

4.4. Comparison of Internal and External Water Effect on Coal Gasification and Combustion. The previous measurement results indicated that the effects of water on coal gasification and combustion are obvious. Therefore, in this section, coal water mixtures were investigated by not only different water/coal mass ratio but also different states of internal and external. In the case of Coal no. 2, coal-water mixture was made by 20 mg of dried coal with different quantity of water (2~12 mg). But for Coal no. 3, it was made by water evaporation from saturated Coal no. 3 sample with elapsed time in sealing dried air chamber as shown in Figure 4. In the measurements, gas concentrations of CO and HCs generated in CO₂-rich with 5% and 10% O₂ atmospheres are shown in Figures 16 and 17 to discuss the effects of water/coal mass ratio on the coal samples. The water/coal mass ratio has an interesting function to CO and HCs gas generations regardless of their states, but not for coal weight reduction ratio.

Comparison results indicated that coal sample with internal water made larger differences with 5% and 10% O₂ on CO and HCs gas generations under the same condition

of laser beam power of 10 W. However, the external water on coal samples caused little differences with 5% and 10% O₂ on CO and HCs gas generations, especially for water/coal mass ratio of 20~35%, that is, the optimum proportion extent. In addition, generating amount of CO gas is decreased with increasing water/coal mass ratio in the conditions of 5% and 10% O₂; on the contrary, generating amount of HCs gas is increased with increasing water/coal mass ratio in the atmospheres of 5% and 10% O₂. These measurement results imply that steam has an important role for gas productions gasified with 10% O₂, especially for 5% O₂.

5. Conclusions

In this study, coal combustion and gasification properties of Datong coal have been investigated by rapid heating with the CO₂ laser beam. Coal weight reduction ratio or 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 (50 to 200°C·s⁻¹) of dry, wetted coal and mixing coal-water samples, it is expected that internal water and external water on coal particles have an interesting function to make increase generation of HC gas and decrease of CO gas by promoting chemical reactions between coal or char and H₂O. Consequently, a possibility has been shown to accomplish coal gasification process with easier CO₂ capture by replacing air with CO₂ in considering water effects.

The present study is summarized as follows.

- (1) Coal weight reduction ratio of Coal no. 1 in O₂-rich atmosphere with 10% O₂ was increased from 38.7% to 42.1% compared with the case of 5% O₂ under the same condition of laser beam power of 10 W. Furthermore, the one of dry coal by mixing water (Coal no. 2) was increased from 42.1% to 47.2% with the case of 10% O₂ and laser power of 10 W. The coal weight loss against temperature followed the Arrhenius equation.
- (2) CO gas generation mainly depends on coal temperature and CO₂ concentration, while HC gas generation relies on O₂ concentration and H₂O. Further, coal and char gasification with O₂ gas is in a dominant position comparing with water vapor for the case of 10% O₂; however, partial water vapor substitutes the role of O₂ gas to participate in coal and char gasification when O₂ concentration is 5%.
- (3) CO/CO₂ reaction ratios of coal and char were evaluated as 1 : 2.0 and 1 : 2.8 in the atmosphere of 5% O₂ with laser power of 10 W, respectively. In addition, HCs gases of coal and coal water mixture were mainly specified with volatile matter of coal.
- (4) Generating amount of CO gas was decreased with increasing water/coal mass ratio with 5% O₂; on the contrary, generating amount of HC gas was increased by increasing water/coal mass ratio for 10% O₂.

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