Korean J. Chem. Eng., **24**(3), 489-494 (2007)

Catalytic coal partial gasification in an atmospheric fluidized bed

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(*Received 22 August 2006 • accepted 11 November 2006*)

Abstract−The coal partial gasification catalyzed by limestone, sodium carbonate and dolomite was studied using a bench-scale atmospheric fluidized bed in the presence of air and steam at 900 °C. The effects of limestone, sodium carbonate and dolomite on composition, heating value, gas yield of product gas and carbon conversion in the catalytic coal partial gasification have been examined. The experimental results show that the catalysts can effectively improve the gas quality, the heating value and the gas yield of product gas and carbon conversion. The catalytic effect of sodium carbonate is better than that of limestone and dolomite. The increase of limestone loading can enhance the quality of product gas, such as the content of combustible gas, the high heating value and the gas yield, during coal partial gasification.

Key words: Coal, Partial Gasification, Catalyze, Fluidized Bed

INTRODUCTION

At present, insufficient supply and increasing price of fossil fuels such as coal and oil has led to an energy crisis throughout the world. Great importance has been attached to the research and development of high-efficiency and low-emission conversion technology of conventional fuels [1]. Clean coal technology based on coal partial gasification and residual char combustion is one of the multistage conversion technologies for “dirty” coal that has high ash content and high ash melting point, and is also considered as one of the promising clean coal technologies. As for the clean coal technology, the high activity compositions in “dirty” coal first gasify into a combustible gas in the product gas, and then the residual low activity chars combust in the combustion chamber to supply heat or generate power, which can realize the purpose of coal utilization with high efficiency and environmental performance and reduce the gross investment and the operating cost of a coal-fired plant [2-4].

The catalytic gasification of coal has been extensively studied throughout the world in recent twenty years because of its numerous advantages of (1) fast gasification reaction rate [5], (2) high carbon conversion [6], (3) low reaction temperature [7], (4) low pollutant emission [8], and (5) different gasification products (such as syngas, oil, and other chemical materials) [9]. However, less attention has been paid to the catalytic coal partial gasification in an atmospheric fluidized bed.

The effect of air/coal ratio, steam/coal ratio, bed temperature, and coal rank on the composition, high heating value (HHV), gas yield of product gas and carbon conversion during the coal partial gasification has been reported elsewhere [2]. According to a previous coal partial gasification test, the HHV and gas yield of product gas and carbon conversion are not high enough [2]. Therefore, it is very necessary to improve the quality of product gas and the gasification efficiency during the coal partial gasification in a fluidized bed. The purpose of this study was to investigate the effects of three catalysts including limestone, sodium carbonate and dolomite on coal partial gasification in a bench-scale atmospheric fluidized bed in the presence of air and steam at 900 °C.

EXPERIMENT

1. Materials

The coal used in the experiment is Xuzhou bituminous coal. Its mean particle size is 0.56 mm. Table 1 shows the proximate and ultimate analysis of coal. Quartz sand is used as the inert bed material and its average particle size is 0.58 mm. The major composition of Nanjing limestone and Nanjing dolomite is shown in Table 2.

2. Experimental Apparatus

Fig. 1 shows a schematic diagram of the fluidized bed system for coal partial gasification in this study. The whole system consists of subsystems of a start-up burner, air supply, steam generator, coal feeding, measurement and control, and a fluidized bed gasifier. The gasifier with an inner diameter of 100 mm and a height of 4.4 m is made of the refractory stainless steel. The coal feeding subsystem consists of a frame, a hopper, an electric motor and a speed controller. The cold air from the blast blower is divided into two currents: one supplies the oxygen for the combustion of diesel oil in the start-up burner and then enters the interlayer to heat the gasifier, and the other is preheated by the heat exchanger placed in the start-up burner, enters the gasifier to fluidize the bed material and supplies the reagents for coal gasification after mixing with the steam generated from the steam boiler. At the top of gasifier, the primary cyclone allows the recovery of entrained particles. Temperature probes and pressure gauges are placed along the height of

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[‡] This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

Table 1. Proximate and ultimate analysis of Xuzhou bituminous coal

Ultimate analysis (wt%)					$Q_{net.ar}$	Proximate analysis (wt%)			
C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}	(MJ/kg)	A_{ad}	M_{ad}	V_{ad}	FC_{ad}
70.40	4.54	7.86	1.24	0.63	28.91	12.62	2.72	30.57	54.09

Table 2. Composition of limestone and dolomite (wt%)

Composition	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3
Limestone	51.22	0.31	3.76	1.45	0.45
Dolomite	30.08	20.38	1.56	0.48	0.32

gasifier and product gas pipe. There is a sampling port of product gas downstream of the secondary cyclone.

Each run was started with the filling of the bed of quartz sand up to the required height. The screw feeder was turned on and the minimum fluidizing air flow rate required to fluidize the bed material in the gasifier was supplied through the diesel oil start-up burner. It was necessary to preheat the gasifier up to the required temperature before the commencement of coal feeding. When the bed temperature reached 600 °C, coal was fed into the gasifier by a screw feeder and the coal feeding rate was adjusted to allow a certain excess air in order to achieve complete combustion of coal. When the bed temperature in the gasifier met the demand of coal gasification, the air, steam and coal flow rates were adjusted to give the desired equivalence ratio. The gasifier operated at the steady state condition for an hour. The pressure loss and the temperature were monitored and registered at a 10 minutes interval. After the bed temperature stabilized, the product gas sample was collected to analyze. The screw feeder was stopped once the sample collection and data recording was completed. The whole fluidized bed coal gasification system was shut down after the temperature dropped below the safe temperature.

3. Sample Analysis

The product gas sampled from the downstream of the secondary cyclone was sent to analyze the composition of product gas by a gas chromatography. The chromatography calibration was done with a standard gas and the standard deviation curve of the typical composition was drawn. Argon was used as the carrier gas at a flow rate of 44 mL/min. The temperature of chromatography column, which is made of stainless steel, 4 m×3 mm i.d., and with TDX-01 (80-100 meshes) as stationary phase, was 80 °C, and that of the thermal conductivity detector (TCD) was 120 °C.

4. Data Processing

The HHV of product gas is defined as follow:

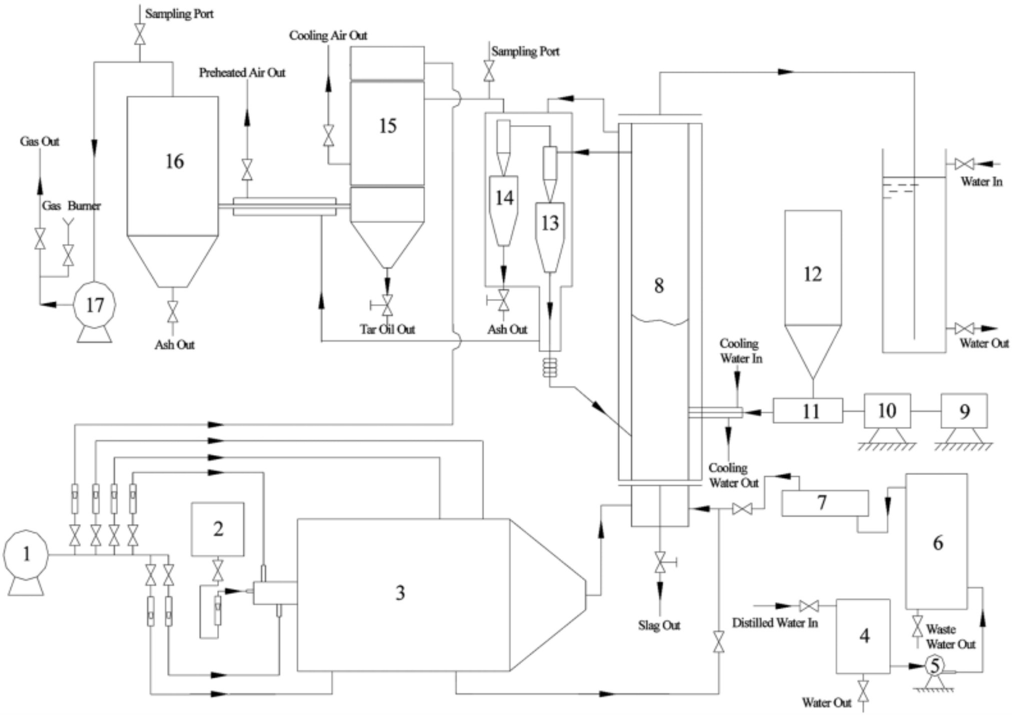


Fig. 1. The schematic diagram of the test facility.

1. Blast blower
2. Diesel oil tank
3. Start-up burner
4. Water tank
5. Water pump
6. Steam boiler
7. Steam superheater
8. Fluidized bed gasifier
9. Electric motor
10. Speed controller
11. Screw feeder
12. Coal feeding copper
13. Primary cyclone
14. Secondary cyclone
15. Removal tar tower
16. Bag house
17. I.D. fan

$$\mathrm{HHV} = (X_{CO}\times 3,018 + X_{H_2}\times 3,052 + X_{CH_4}\times 9,500)\times 0.01\times 4.2\ (\mathrm{kJ/Nm^3}) \quad (1)$$

where, X_{CO}, X_{H_2}, X_{CH_4}, are the volumetric percentage of CO, H_2, CH_4 in product gas, respectively.

The dry gas yield, Y, is figured out from the material balance of nitrogen:

$$Y = \frac{Q_a \times 79\%}{W_C X_{N_2}\%}\ (\mathrm{Nm^3/kg}) \quad (2)$$

where, Q_a is the flow rate of air (Nm^3/kg), W_C is the coal feed rate (kg/h), X_{N_2} is the volumetric percentage of N_2 in product gas.

The carbon conversion is calculated by,

$$X_C = \frac{12 \times Y \times (CO\% + CO_2\% + CH_4\%)}{22.4 \times C\%} \times 100\% \quad (3)$$

where, Y is the dry gas yield (Nm^3/kg), C% is the mass percentage of carbon in coal ultimate analysis, the other symbols are the volumetric percentage of product gas compositions.

RESULTS AND DISCUSSIONS

The factors including the air/coal ratio, the steam/coal ratio, the bed temperature, and the catalyst loading greatly affect coal partial gasification. For the purpose of comparison, the catalytic coal partial gasification was carried out in a bench-scale atmospheric fluidized bed gasifier. The limestone, sodium carbonate and dolomite were blended with coal, and their loadings were all 3 wt%. Coal partial gasification without catalyst was conducted. In a series of tests, the air/coal ratio (2.82 Nm^3/kg), the steam/coal ratio (0.39 kg/kg), the bed temperature (900 °C) and the bed height (300 mm) were kept constant.

The effect of the three catalysts on gas compositions of product gas is presented in Fig. 2. They have a significant effect on coal partial gasification. It can be seen that they can increase the product gas quality and the content of combustible compositions including carbon monoxide, hydrogen and methane in product gas. The order of their catalytic effect was: sodium carbonate>limestone>dolomite. In 1921, Taylor started to study the effect of catalysts on coal gasification and found that sodium carbonate is the effective catalyst for the gasification reaction of coal [10]. Once it is fed into the gasifier, sodium carbonate first reacts with carbon to produce carbon monoxide and sodium, and the sodium enters into gas phase and arbitrarily reacts with carbon dioxide to produce carbon monoxide and sodium oxide, and then the sodium oxide further react with carbon dioxide to produce sodium carbonate. Oxidative-reduction cycles of sodium carbonate appear to be the best explanation of its catalytic activity. The above reactions are shown as follows: $Na_2CO_3+2C\rightarrow 2Na+3CO$, $2Na+CO_2\rightarrow Na_2O+CO$, $Na_2O+CO_2\rightarrow Na_2CO_3$. However, Xie and Suzuki [11] thought that sodium carbonate does not directly react with carbon or carbon dioxide. Sodium carbonate can change the partitioning of electron cloud on the surface of char, make stronger active sites on the surface of char, reduce the intensity of C-C bond and make the gasification reaction of carbon and carbon dioxide easier. Though the above viewpoints are different from each other, the final results are the same in terms of increasing the content of combustible components in product gas. Zhu [12] found that lime can not only enhance the gas yield but also reduce the tar yield. Lime has a strong catalytic effect on the tar formed during coal gasification and can improve evidently the content of carbon monoxide, hydrogen and methane in product gas. Feng [13] researched the catalytic effect of limestone on coal gasification with the presence of steam and found limestone can increase the gasification reaction rate of coal and steam. The effect of calcium compound on coal gasification is different from that of sodium compound. The catalytic mechanism of calcium compound can be presented as follows: $Ca_nO_m+CO_2\rightarrow Ca_nO_{m+1}+CO$, $Ca_nO_{m+1}+C\rightarrow Ca_nO_m+CO$. David [14] thought dolomite could increase the gas yield at the expense of liquid products and the main function of dolomite is to act as a guard bed for the removal of heavy hydrocarbons prior to the reforming of higher hydrocarbons to produce a product gas of syngas quality. Interestingly, it can be seen that the composition of limestone is similar to that of dolomite in Table 2. That is, the main composition of limestone and dolomite is calcium oxide. Therefore, the catalytic mechanism of dolomite is similar to that of limestone. The difference between limestone and dolomite is that the content of magnesia (MgO) in dolomite is higher than that in limestone. However, the sum of the content of magnesia and calcium oxide in dolomite is nearly equal to the content of calcium oxide in limestone. It can be also found that the cat-

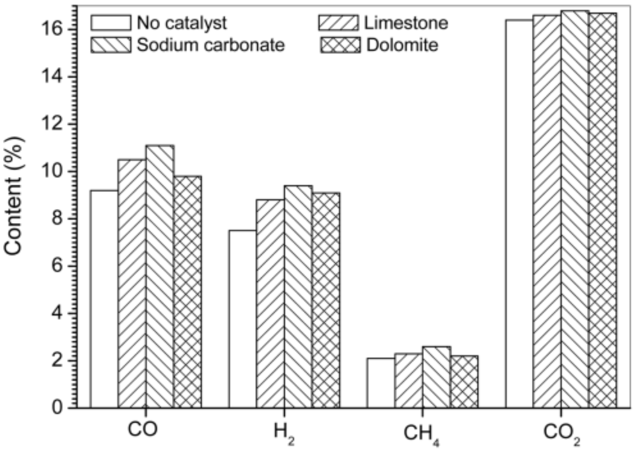


Fig. 2. Effect of catalysts on gas composition.

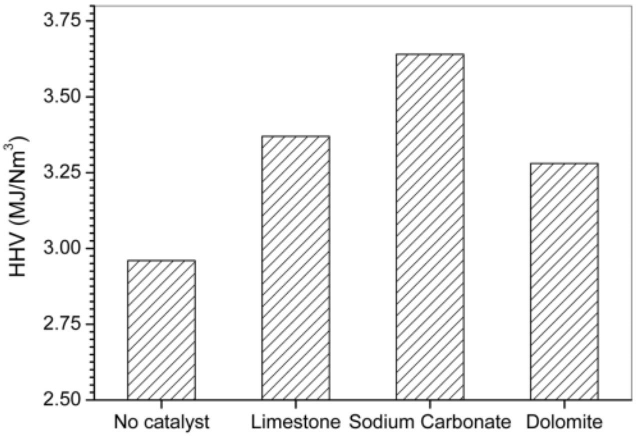


Fig. 3. Effect of catalysts on gas HHV.

alytic effect of dolomite is lower than that of limestone in Fig. 2. Therefore, it may be concluded that the catalytic effect of calcium oxide on coal gasification is higher than that of magnesia.

The effect of the three catalysts on HHV of product gas was also investigated in this study. The results are illustrated in Fig. 3. Compared with the non-catalytic coal partial gasification, it can be found that the feed of limestone, sodium carbonate and dolomite can increase the gas HHV by 13.85%, 22.97% and 10.81%, respectively. However, the HHV of product gas with the presence of catalyst is between 3.28 MJ/Nm^3 and 3.64 MJ/Nm^3. From Fig. 3, it can also be seen that though they can increase the gas HHV by 10.81-22.97%, the HHV of product gas with the presence of catalysts is not high enough because the HHV of product gas without catalysts is only 2.96 MJ/Nm^3. The reason for the low HHV of product gas without catalysts is that the large quantity of nitrogen introduced into gasifier with fluidizing air will carry the caloric out and reduce the content of the combustible compositions in product gas during coal partial gasification with the presence of air and steam. The elutriation and entrainment of the fine coal particle, the caloric losses through the walls and the bare flanges, and the short residence time of coal particle in the gasifier can also make the HHV decrease.

Due to the high temperature and large flow rate of product gas at the exit of the fluidized bed gasifier, it is difficult to measure the gas yield. However, compared with the nitrogen content in air, the nitrogen in coal is low; thus, the dry gas yield can be calculated by the nitrogen equilibrium during coal partial gasification. Compared with the non-catalytic coal partial gasification, the yields of product gas can be increased by 6.16%, 9.71% and 5.50%, respectively, by feeding limestone, sodium carbonate and dolomite (shown in Fig. 4).

Like the combustion of coal in a fluidized bed, the carbon conversion efficiency of coal partial gasification in a fluidized bed gasifier also depends on the carbon content of fly ash and bottom ash and the percentage of fly ash and bottom ash in total ash. Fig. 5 shows the effect of limestone, sodium carbonate and dolomite on the carbon conversion during coal partial gasification in fluidized bed gasification. It can be concluded that, compared with the non-catalytic coal partial gasification, the carbon conversions of coal partial gasification increase by 11.38%, 18.34% and 7.92%, respectively, by feeding limestone, sodium carbonate and dolomite. The reason is that the increase of the content of combustible compositions and the yield of product gas must lead to the increase of carbon conversion. The carbon conversion is between 68.53% and 81.10% during coal partial gasification in a fluidized bed gasifier. The reason for low carbon conversion is similar to that of low HHV of product gas, that is, the elutriation and entrainment of the fine coal particle without a circulating device for fine bed material, the heat losses through the walls and the bare flanges, and the short residence time of coal particles in the gasifier can also make carbon conversion decrease.

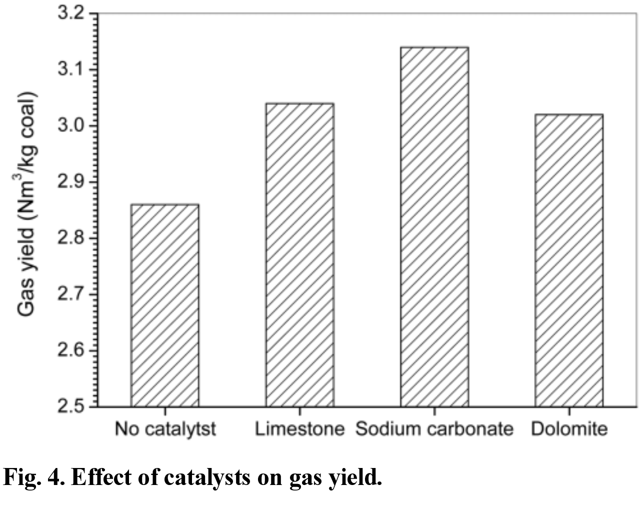


Fig. 4. Effect of catalysts on gas yield.

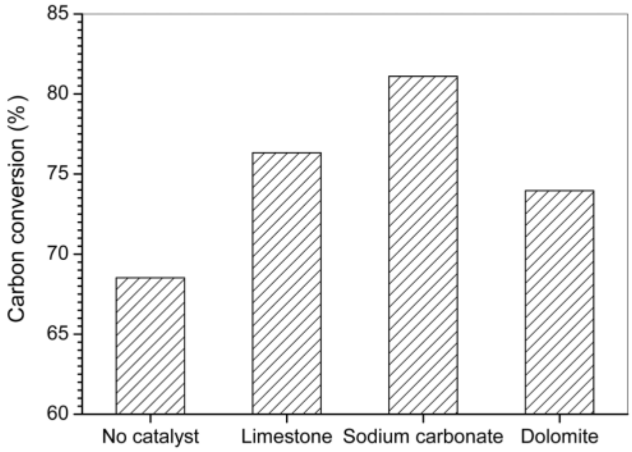
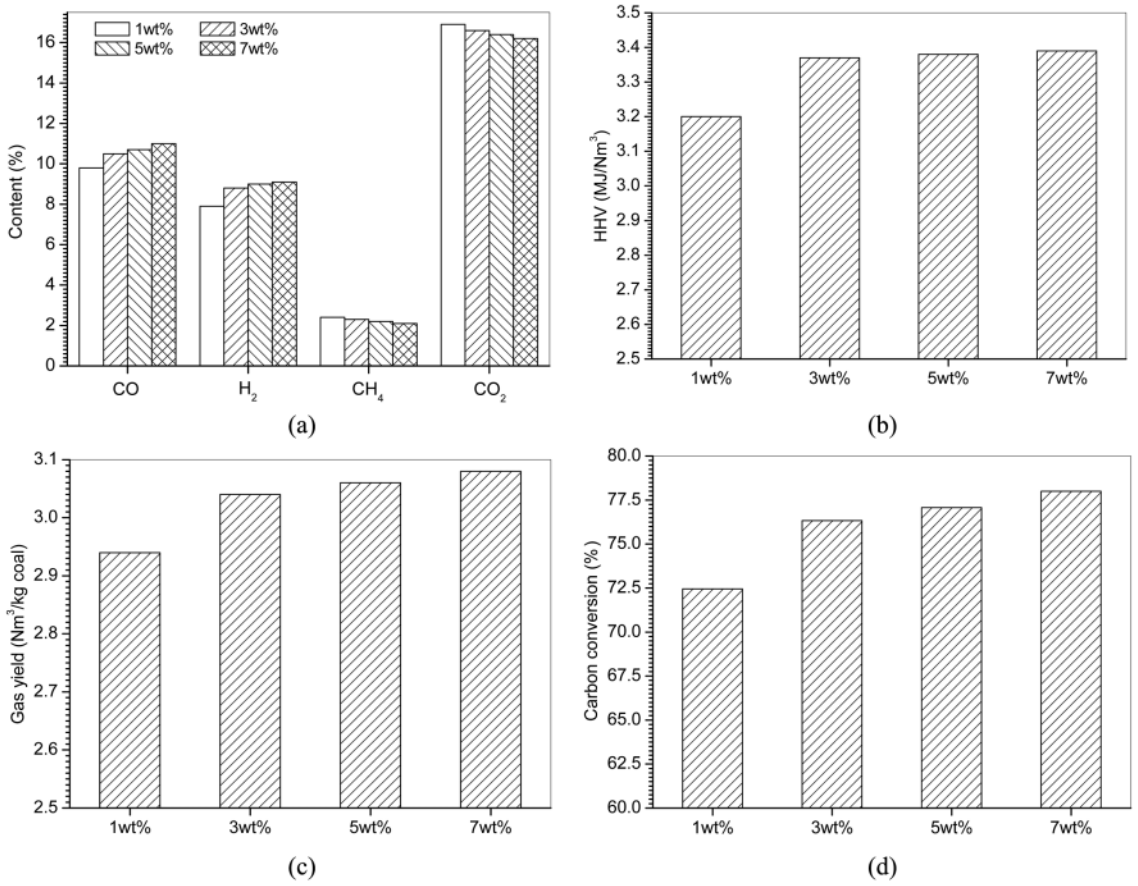


Fig. 5. Effect of catalysts on carbon conversion.

The experiment of the effect of limestone loading on coal partial gasification was performed in a bench-scale atmospheric fluidized bed gasifier. In the catalytic coal partial gasificatiom experiment, the limestone loading varied from 1 wt% to 7 wt% while the air/coal ratio (2.82 Nm^3/kg), the steam/coal ratio (0.39 kg/kg), the bed temperature (900 °C) and the bed height (300 mm) remained unchanged. The experimental results of the effect of limestone loading on the quality of product gas are plotted in Fig. 6.

Fig. 6 shows that the content of carbon monoxide and hydrogen increases and that of carbon dioxide and methane decreases by varying the limestone loading from 1 wt% to 7 wt% during coal partial gasification in fluidized bed. Once it feeds into the gasifier, the limestone will be rapidly pyrolyzed into lime and carbon dioxide. By enhancing the coal gasification reaction rate, the lime has a good catalytic effect on the tars formed during coal partial gasification and can improve obviously the content of combustible components such as carbon monoxide and hydrogen in product gas. The content of methane can also be increased slightly with the presence of catalyst (shown in Fig. 2). However, the methane mainly originates from the pyrolysis of volatile matter in coal. The slight decrease of the content of methane in Fig. 6 may be the result of the increase of gas yield. In addition, the increase of limestone loading can improve the probability of catalytic coal gasification reaction; thus, it favors the increase of the content of carbon monoxide and hydrogen in product gas. From Fig. 6, it can be concluded that the HHV of product gas increases with the increase of limestone loading. However, the increasing extent of gas HHV is small when the limestone loading increases from 1 wt% to 7 wt%. The HHV of product gas is closely related to the content of combustible compositions in product gas. The increase of the content of combustible composi-



(a) (b)

(c) (d)

Fig. 6. Effect of limestone loading on coal partial gasification.

tions must result in the HHV of product gas increase. The purpose of the feed of limestone is to accelerate the coal partial gasification in this study. The fast reaction rate favors the oxidation reaction ($C+0.5O_2 \rightarrow CO$) leading to the increasing of carbon monoxide, the boudouard reaction ($C+CO_2 \rightarrow 2CO$) leading to the increasing of carbon monoxide, the water gas reaction ($C+H_2O \rightarrow CO+H_2$) leading to the increasing of carbon monoxide and hydrogen, and steam decomposing reaction. The gas yield during coal partial gasification must be increasing with the increase of combustible compositions such as carbon monoxide and hydrogen. Therefore, the increase of limestone loading can make the gas yield increase (shown in Fig. 6). With the simultaneous increases of the content of carbon monoxide and hydrogen, and the gas yield, it can be found that the carbon conversion of coal partial gasification also increases with the increase of limestone loading in Fig. 6.

CONCLUSIONS

The catalytic coal partial gasification in an atmospheric fluidized bed gasifier was performed in this study. Compared with the non-catalytic coal partial gasification, sodium carbonate, limestone and dolomite have an obvious catalytic effect on coal partial gasification. They can effectively improve composition, heating value, yield of product gas and carbon conversion during coal partial gasification. However, the catalysts have different catalytic effects on coal partial gasification. The catalytic effect of sodium carbonate is better than that of limestone and dolomite. The increase of limestone loading can increase the content of combustible compositions, the high heating value and the gas yield in product gas, and the carbon conversion during coal partial gasification in a fluidized bed gasifier.

ACKNOWLEDGMENT

The authors acknowledge the support received for this research from the Key Project of State Basic Study of Ministry of Science and Technology of China, the National Natural Science Fundational of China (Grant No. 50608040), the "Qinglan Gongcheng" of Jiangsu Province, and the Foundation of Science & Research of Nanjing University of Information Science & Technology.

REFERENCES

1. Z. Tang and Y. Wang, *Fuel Process. Technol.*, **62**, 137 (2000).
2. H. C. Zhou, B. S. Jin, Z. P. Zhong, Y. J. Huang and R. Xiao, *Energy Fuels*, **19**, 1619 (2005).
3. R. Xiao, M. Y. Zhang, B. S. Jin, Y. J. Huang and H. C. Zhou, *Energy Fuels*, **20**, 715 (2006).
4. O. Shinada, A. Yamada and Y. Koyama, *Energy Convers. Manage.*, **43**, 1221 (2002).
5. S. F. Li and Y. L. Cheng, *Fuel*, **74**, 456 (1995).
6. Y. S. Yun and Y. D. Yoo, *Korean J. Chem. Eng.*, **18**, 679 (2001).
7. W. J. Lee, S. D. Kim and B. H. Song, *Korean J. Chem. Eng.*, **18**,

640 (2001).

8. R. C. Brown, Q. Liu and G. Norton, *Biomass Bioenergy*, **18**, 499 (2000).
9. R. Sineenat, M. Lursuang, K. Prapan and P. Pornpote, *Korean J. Chem. Eng.*, **23**, 216 (2006).
10. X. F. Zhao, L. Y. Yang and Z. H. Shi, *Coal Technol.*, **24**, 103 (2005).
11. K. C. Xie, *Coal structure and its reactivity*, Science Press, Beijing (2002).
12. T. Y. Zhu, L. P. Liu, Y. Wang and J. J. Huang, *J. Fuel Chem. Technol.*, **28**, 36 (2000).
13. J. Feng, W. Y. Li and K. C. Xie, *J. Taiyuan Univ. Technol.*, **27**, 50 (1996).
14. S. David, K. Brian and R. H. R. Julian, *Fuel Process. Technol.*, **69**, 29 (2001).