Korean J. Chem. Eng., **24**(3), 508-511 (2007)

Co-pyrolysis characteristics of coal and natural gas

Lirong Kang, Jianmin Zhang†, Hui Lian and Ming Luo

College of Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
(*Received 26 August 2006 • accepted 1 November 2006*)

Abstract−A co-pyrolysis experiment of coal and natural gas was investigated on a fixed-bed reactor. SEM was used to study the structure changes of the exterior surface of char prepared in this co-pyrolysis experiment, while GC was also utilized to analyze the associated gas. The result showed that, with increasing temperature, the coal char tended to agglomerate. GC and SEM results show that the CH_4 decomposition on the exterior surface of char was turned to filamentous char and extended around like coral. It was also proved that the co-pyrolysis of coal and natural gas promoted syngas production. A synergistic effect of coal and natural gas does exist during this process.

Key words: Coal and Natural Gas, Co-pyrolysis, Syngas, Char, Synergistic Effect

INTRODUCTION

As a clean and high efficiency energy, natural gas has been widely used in many developed countries. However, in China, natural gas only claims about 3% of whole energy consumption, while coal accounts for 70% and the petroleum is limited. At present, it's the main restriction for chemical product development because of expensive and scanty natural gas, which has been the main feedstock for that for many years. Considering the unbalance between energy source and serious pollution problem, it's a trend for coal access to chemical field to meet the needs in future.

Syngas is mostly approach to chemical combination, which from nature gas has high H/C ratio. That from coal gasification is lower. All the syngas is unfit for the subsequent chemical synthetic process. Co-conversion concept comes to mind for it not only solves the H/C ratio problem but also fully makes use of the natural gas and the abundant coal resources in China.

Coal pyrolysis exhibits great changes in different atmosphere including N_2, CH_4, and CO_2 etc. Some researchers found coal pyrolysis in reductive atmosphere can change the rules of volatile gas and polluted element being emitted. Sineenat Rodjeen also discovered that the pyrolysis of coal-biomass mixtures plays an important role in gas synthesis in certain conditions [1].

In this paper, we studied the co-pyrolysis behavior of coal and natural gas to determine whether there is synergistic effect during this process.

EXPERIMENTAL

A study of coal pyrolysis was performed on a fixed-bed reactor with an inside diameter of 25 mm and length 1.08 m in the atmosphere of N_2 and natural gas. The char samples and associated gas, which are collected during the experiment, were investigated by the SEM and GC, respectively.

†To whom correspondence should be addressed.
E-mail: founderzhang@hotmail.com
‡This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

Table 1. Longkou lignite's proximate analysis and ultimate analysis

Ultimate analysis Wad/%					Proximate analysis Wad/%			
C	H	O	S	N	M	A	V	Fc
60.01	4.39	14.46	0.62	1.54	1.42	17.56	36.20	44.82

Table 2. The composition of natural gas V/%

Composition	CH_4	N_2	CO_2	C_2H_4	C_2H_6	C_3H_8
Concentration (V/%)	80.00	4.49	5.00	9.57	0.83	0.11

The coal samples were Longkou lignite; the proximate analysis and ultimate analysis were given in Table 1. The composition of natural gas is shown in Table 2.

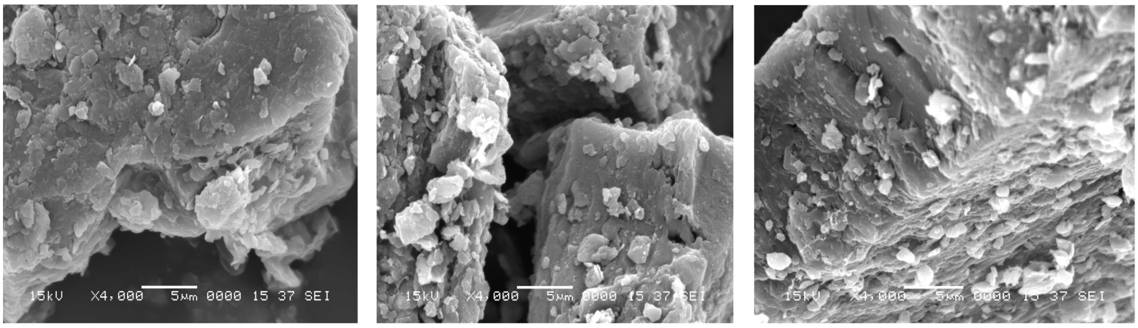
Pyrolysis experiments were carried out on fix-bed furnace; following is the process. First, the natural gas or nitrogen gas controlled by mass meter passes through the coal sample placed in the tube furnace; the flux is 300 SCCM (standard cubic centimeter per minute), and the temperature was programmed controlled from 100 °C to a terminal temperature in the rate of 20 °C/min and then held for ten minutes. During the 10 minutes, a gas sample was collected and analyzed through the Gas Chromatograph (GC). The coke samples were collected after the furnace was cooled by nitrogen and used for the Scanning Electron Microscopy (SEM) study.

RESULTS AND DISCUSSIONS

1. The Characteristics of Char

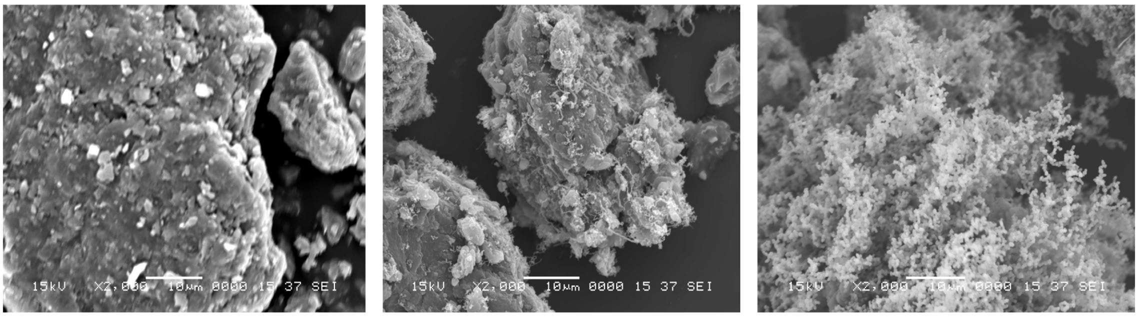
Coal gasification mainly involves two steps: initial rapid devolatilization of coal to produce char, tar and gases and subsequent gasification of the char generated [2]. Char gasification, being the slow step, usually controls the overall conversion process, and a better understanding of char structure varieties is essential to understand the behaviors of coal pyrolysis in two different ambiences.

From the macrographs of char prepared at 800 °C, 900 °C, 1,000 °C, 1,100 °C, 1,200 °C in nitrogen atmosphere, we can observed that it's no big difference, but by keeping the powder state on ex-



(a) (b) (c)

Fig. 1. The SEM photographs of char prepared in nitrogen atmosphere.



(A) (B) (C)

Fig. 2. The SEM photographs of char prepared in natural gas atmosphere.

terior images for the char prepared before 1,100 °C, only from that on, do some small particles appear and more until 1,200 °C. But we found that the phenomenon of agglomeration was not so obvious at different temperatures. Comparing the macrographs of char prepared in natural gas atmosphere, the characteristics of char are different from that in nitrogen atmosphere. The latter tends to agglomerate together with enhancing terminal temperature. It changes from powder to agglomeration at 1,000 °C, even to hardening at 1,200 °C, which shows a striking contrast with the state at 800 °C. The whole level of agglomerate is more severe and bigger than that in nitrogen atmosphere.

Fig. 1 shows the SEM photographs of char produced separately at 800 °C (a), 1,000 °C (b), 1,200 °C (c) in the nitrogen atmosphere from left to right, which are magnified 4,000 times.

Fig. 2 shows the SEM photographs of char produced separately at 800 °C (A), 1,000 °C (B), 1,200 °C (C) in the natural gas atmosphere from left to right, which are magnified 2,000 times.

Some more details can be observed on SEM photographs in Fig. 1 and Fig. 2. We noticed that it's difficult to find particles on the surface of char produced at 800 °C in nitrogen atmosphere (a), only a few till 1,200 °C (c). However, Fig. 2 shows deposited particles become more and more and tend to develop silkiness with increasing pyrolysis temperature at last.

The reason why the particles generate and increase perhaps is that coal maceral concentrates slowly from original unordered state to agglomerate, with the enhancing of temperature and the release of volatile gas, from small particulates into a cluster of particles.

Fig. 2(C) shows the exterior carbon tubes take on a slight transparent colour, which will enrich enormously the micropore structure on char surface if they are hollow. We suppose it's the truth, that they are propitious for producing char with strong absorptive capacity. The above views await to be identified in future experiments [3-5].

2. Gas Analysis

2-1. The Component Analysis of Syngas Produced in Nitrogen Atmosphere

The pryrolysis experiments were carried out in nitrogen atmo-

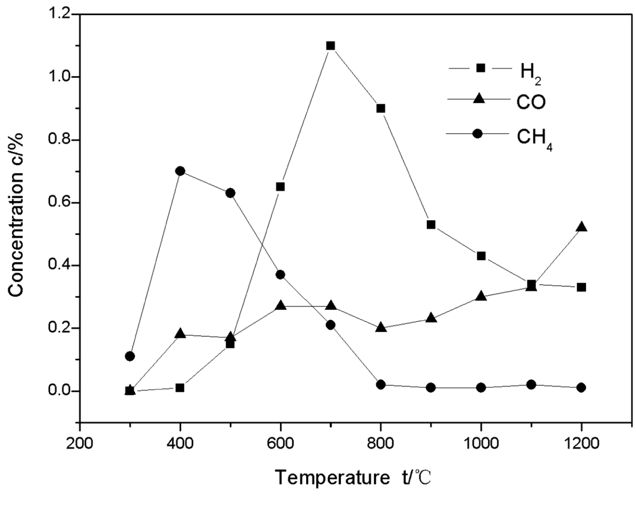


Fig. 3. The concentration of H_2, CH_4 and pyrolysis temperature in nitrogen atmosphere.

sphere, with the pyrogenation gas containing CH_4, CO, H_2, CO_2 etc., which were collected to analyze by GC.

Fig. 3 shows the relationships between the concentration of CH_4, CO, H_2 and temperature variation in nitrogen atmosphere. We notice that the concentration of CH_4 is present at 300 °C and increases gradually to a maximum at 400 °C, which is approximately 0.7%, then declines slowly to disappear at 800 °C. The above CH_4 is from the cracking of aromatic hydrocarbon side chain in coal; this happened at a low temperature. With increasing temperature, the short side chains and the bridge bonds connecting an aromatic ring, which have higher thermal stability, in the condensed aromatic rings also start to break up, and the higher the temperature, the slighter for relative molecular weight of released gaseous products. It becomes only H_2 from 750 °C. Consequently, we can observe the concentration of H_2 is present from increasing to reducing successively and reaches to maximal 1.1% at 700 °C. H_2 was observed during the whole pyrolysis process; indeed, a portion of it comess from the cracking of CH_4. That's why the concentration of CH_4 disappears after 800 °C. It's a condensed process to coal pyrolysis. Along with the rupture of side chains and the bridge bonds, the carbon net extends and H_2 is emitted continuously. When it reaches a higher temperature, the condensation process in interior char tends to change down and there is a reduction of amounts of broken chains and bonds, the same as H_2 [6].

About the variation of CO concentration: it is increasing with enhancing the temperature except for some slight discordance between 700 °C to 1,000 °C. It reaches to maximal 0.52% at 1,200 °C. CO is completely from the coal pyrolysis in nitrogen atmosphere. The cracking of carbonyl and the disconnection of oxygen heterocycle are the main sources; the former happens at about 400 °C and the latter needs in excess of 500 °C. In addition, it's also possible that CO originated from the decomposition of bridge bonds [7].

2-2. The Component Analysis of Syngas Produced in a Natural Gas Atmosphere

Fig. 4 shows the concentration of CH_4 approaches to 80% around 700 °C and goes down from that. From previous experiment we determined that CH_4 itself did not decompose below 950 °C. But it

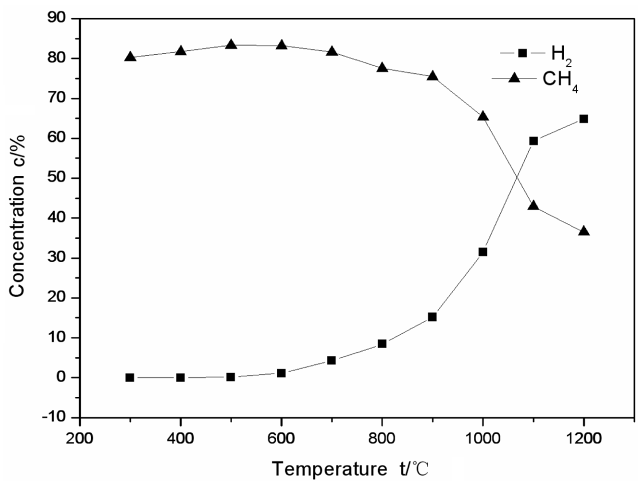


Fig. 4. The concentration of H_2, CH_4 and Pyrolysis temperature in natural gas atmosphere (the concentration of CH_4 included the effect of atmosphere).

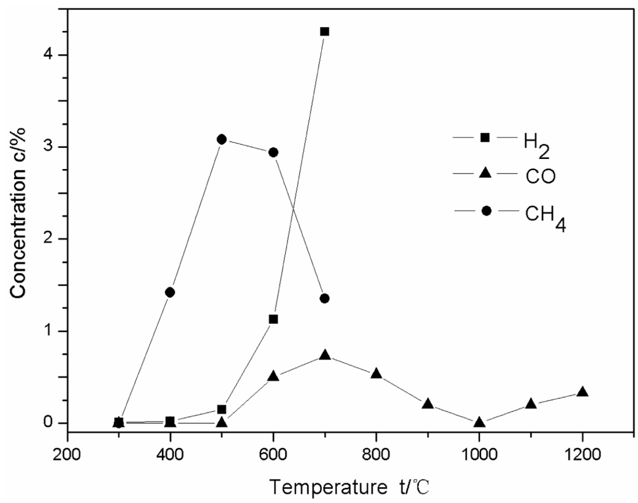


Fig. 5. The concentration of H_2, CO, CH_4 and pyrolysis temperature in natural gas atmosphere (Material natural gas atmosphere has been subtracted from the concentration of CH_4).

began to decompose at 700 °C while the char existed. That indicates it's from the release of coal volatile for exceeding CH_4 before 700 °C, whereas, the reason for decline later is the cracking of CH_4. Beyond that temperature it's difficult to distinguish the origin of H_2. As a consequence, our discussion on the variation of concentration containing CH_4, H_2 is cut off after 700 °C (Fig. 5).

In Fig. 5, we have subtracted the effect of feedstock CH_4 from it as considering the real CH_4 concentration released from coal in natural gas atmosphere. We notice that the concentration of CH_4 released from coal goes up at low temperature, so does that of H_2. But they present an adverse tendency at a temperature greater 700 °C, that of H_2 is going on. Based on the reaction equation CH_4=C+2H_2, the results are almost in accord with the relationships of CH_4 scission reaction in consideration of experimental errors and consumption of H_2 with other matters [8]. We also find that the concentration of CH_4, H_2 released from coal in natural gas atmosphere was more than that in nitrogen atmosphere (Fig. 4 and Fig. 5). Connecting the above results of CH_4 decomposition situation, it indicates that a natural gas atmosphere is favorable to the pyrolysis of coal; more completely to the release of interior volatile gas before 700 °C and more high temperature await more proof. That is also why the H_2 and CH_4 concentration above 700 °C is not displayed.

Fig. 5 also shows the variation of CO concentration in natural gas atmosphere; it is the absence of CO firstly, from 500 °C on, which is increasing rapidly to maximal 0.75%, then goes down quickly and comes back to the first point, increasing again later. Fig. 5 shows the concentration of CO reaches the top point at 700 °C; however, the scission reaction of CH_4 is just starting at that point. It proves that prior CO before 700 °C is originated from coal, not natural gas. Comparing the concentration of CO in two kinds of atmosphere, we find it is two times in natural gas atmosphere than that in nitrogen gas.

CONCLUSIONS

In this work, we have examined the co-pyrolysis characteristics of natural gas and coal, focusing on pyrolysis in nitrogen and natural gas atmosphere. The different varieties on the surface of coal char have been presented in two kinds of ambience from SEM. We also analyzed the effects of syngas resulted by GC.

1. With increasing temperature, the coal char tends to agglomerate under different ambience. GC results show that CH_4 scission reaction is present in natural gas atmosphere. All together, as showed in the corresponding SEM picture, the carbon deposited on the exterior surface of coal char was turned to filamentous coke and extended around like coral.

2. Comparison and analysis have been carried out to the component of coal pyrolysis gas. It was also proved that the co-pyrolysis of coal and natural gas promoted syngas production. A synergistic effect of coal and natural gas does exist during this experiment.

3. 400-700 °C is an optimal temperature range for the interaction of coal and natural gas during co-pyrolysis experiments. It's not apparent for this synergistic effect below 400 °C owing to the low temperature and that of greater 700 °C await more experiment to be investigated.

ACKNOWLEDGMENT

The author would like to thank the support for this work by Shanghai Education Development Foundation for ShuGuang Project under Contract No. 03SG44 and by National Basic Research Program under Contract No. 2004CB217706-03.

REFERENCES

1. S. Rodjeen, L. Mecasut, P. Kuchontara and P. Piumsomboon, *Korean J. Chem. Eng*., **23**, 216 (2006).
2. I. C. Lee, *Korean J. Chem. Eng*., **4**, 196 (1987).
3. A.. A. Herod, M.-J. La'zaro, J. Shearman, J. Card, A. R. Jones and R. Kandiyoti, *Fuel*, **78**, 862 (1999).
4. Y. Yuyum, *Clean utilization of coal*, Dordrecht, Boston, Kluwer Academic (1992).
5. R. A. Schedon, *Chemicals for synthesis gas*, D. Reidel, Publishing Company, Goston (1983).
6. X. Chen, S. Motojimab and H. Iwanaga, *Carbon*, **37**, 1825 (1999).
7. N. R. Hunter, D. Prabawono and H. D. Gesser, *Catalysis Today*, **42**, 347 (1998).
8. Y.-Y. Li, T. Nomurab, A. Sakoda and M. Suzuki, *Journal of Membrane Science*, **197**, 23 (2002).