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Effects of methane concentration on hydrocarbon release during the pyrolysis of coal

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Abstract−The weight-loss characteristics of Longkou lignite were studied by means of thermogravimetric analysis in methane ambience. Pyrolysis experiments of the sample coal in different concentrations of methane were carried out on a tube reactor to study the characteristics of hydrocarbon released. The results show that methane can promote the pyrolysis of lignite in a certain temperature range and the coal can also improve the pyrolysis of methane further. The influence of methane concentration on hydrocarbon release during the pyrolysis of coal is obvious. The hydrocarbon released from the pyrolysis of lignite is intensive within the temperature range from 400 °C to 500 °C and the release of hydrocarbon components dramatically increased as the concentration of methane decreased. This indicates that the release of C_2, C_3 and C_4 has a close relationship with methane pyrolysis and proves that a synergistic effect does exist between the coal and methane.

Key words: Coal, Pyrolysis, Methane, Hydrocarbon, Release

INTRODUCTION

China is rich in coal resources but lacks natural gas; however, direct combustion of coal leads to serious air pollution and natural gas is expensive with its value ever increasing as an alternative fuel [1]. So reducing the direct combustion of coal and improving the utilization of natural gas are leading trends during the energy construction adjusting era. According to the characteristics of rich carbon in coal and rich hydrogen in natural gas, we can make up the defection of each other by using the technique of coal - gas integral conversion, simplifying and optimizing the technique to achieve the conversion and transform integrative. The integrated utilization of coal chemical engineering with natural gas realized the resource reforming and is becoming an important topic in the energy source field. Methane is the primary component of natural gas and coal-seam gas. However, researchers have usually considered methane as an inert gas in pyrolysis, as methane pyrolyzes only at high temperature and paid little attention to the effects of methane on coal pyrolysis [2-4].

The paper studied the weight-loss characteristics of Longkou lignite in methane ambience using thermogravimetric analysis and the pyrolysis characters on a horizontal tube reactor with different concentration of methane. It also analyzed the influence of methane concentration on hydrocarbon releasing during coal pyrolysis and indicates that a synergistic effect does exist between the coal and methane. The active free radicals released from coal pyrolysis promote methane pyrolysis and the active methyl, dimethyl and hydrogen active free radicals given by methane can further promote the coal pyrolysis. At the same time, the release of hydrocarbon accounts for the great deal of active methyl radical, dimethyl and hydrogen active free radicals that were produced, which proves further that a synergistic effect exists between coal and methane. The conclusion supplies support for further research and establishes a new way to use coal, natural gas, coal steam gas effectively and reasonably.

EXPERIMENTAL

The Longkou lignite was used as sample coal in the experiments; the proximate and ultimate analyses of coal are given in Table 1. The Longkou lignite was ground to an average diameter of 50 μm and dried for 60 minutes at 100 °C.

1. Thermogravimetric Experiment

The experiment was carried out on a Computer Differential Thermal Balance (WCT-2A, Beijing optic apparatus company). Each experiment was performed at conditions of 10.0 mg lignite, 60 ml/min gas flux, and heated up to 950 °C with heating rate of 10 °C/min, 20 °C/min, under the pure nitrogen (99.999%) and methane (99.999%) atmosphere. Then the TG curve of the sample coal was drawn by the computer. A schematic of experimental system is shown as Fig. 1.

2. Pyrolysis Experiment

2-1. Pyrolysis Experiment of the Coal

Fig. 2 shows the schematic diagram of the pyrolysis experimental system. The D07-7B/ZM mass flow meter and D08-4/ZM mass flow controller were used in these experiments in order to measure and control the flow accurately. And the gas flux of nitrogen and natural gas is identical in all experiments. First, we set the methane concentration at 3%, 5%, 10% and 20% with nitrogen; the flow was maintained at 300 SCCM (standard cubic centimeter per minute) at atmospheric pressure. We weighed out 1 g lignite and put it into a ceramic vessel, then laid in in the middle of the tube reactor. The mass flow meter was turned on to ensure the mixed methane and nitrogen flowed with certain ratio into the quartz tube. The tube reactor was heated from 100 °C up to 900 °C with the heating rate of

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Table 1. Proximate and ultimate analyses of sample coal

Sample	Ultimate analyses wt/%					Proximate analyses wt/%			
	C	H	O	S	N	M_{ad}	A_{ad}	V_{ad}	FC_{ad}
Longkou lignite	60.01	4.39	14.46	0.62	1.54	1.42	17.56	36.20	44.82

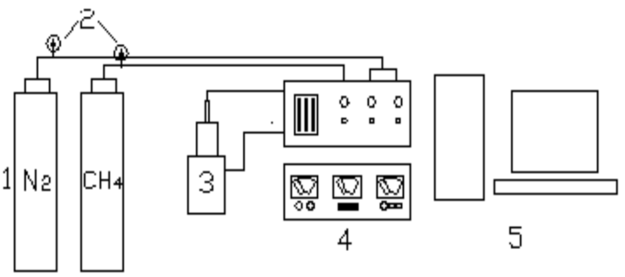


Fig. 1. Schematic diagram of the thermogravimetry experimental system.

1. Cylinder
2. Pressure gauge
3. Thermogravimetric apparatus
4. Thermogravimetric control and display
5. Computer

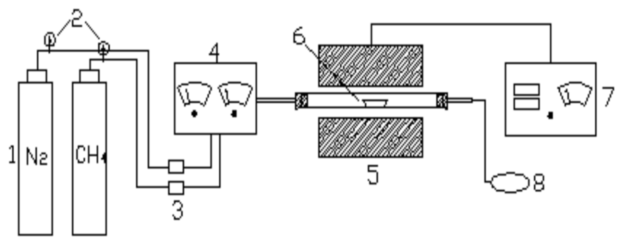
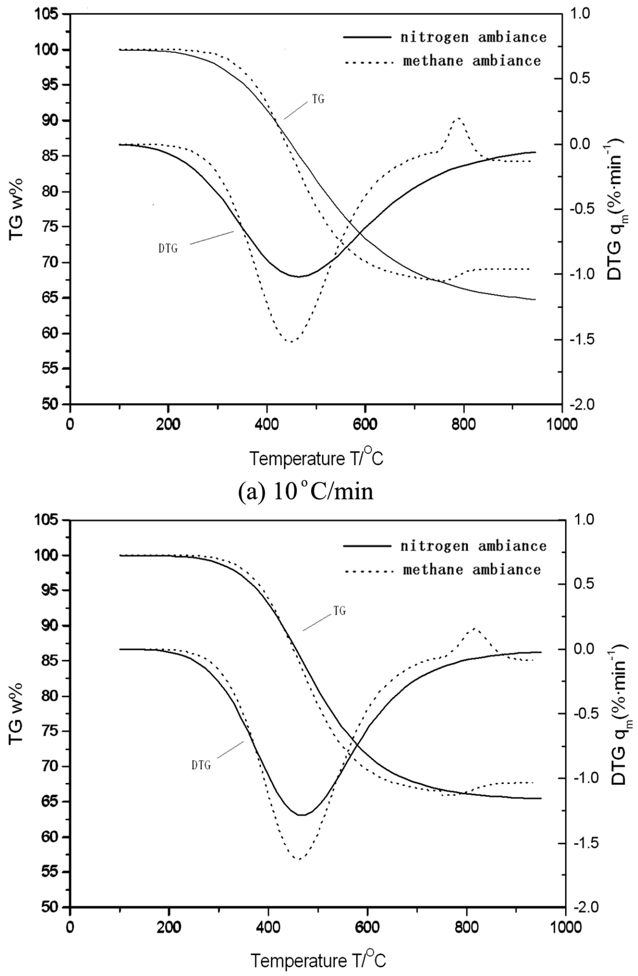


Fig. 2. Schematic diagram of the pyrolysis experimental system.

1. Cylinder
2. Pressure gauge
3. Mass flow meter
4. Mass flow control
5. Tube furnace
6. Ceramic vessel
7. Thermocouple and temperature controller
8. Gas container



(a) 10 °C/min

(b) 20 °C/min

Fig. 3. The TG-DTG curves of lignite pyrolyzed in N_2 and CH_4 ambience with heating rate of 10 °C/min and 20 °C/min.

20 °C/min. The gas product from the coal pyrolysis in each temperature range, such as 200-300 °C, 300-400 °C, 400-500 °C … 800-900 °C, was collected in special bags and analyzed by gas chromatogram.

2-2. Analysis Experiment of Gas Product from the Coal Pyrolysis

The Gas Chromatogram Appearance (GC7890II, Shanghai techcomp science appearance limited company) was used to analyze the pyrolysis gas product. The Al_2O_3 chromatogram volume and FID (Hydrogen Flame Ionization Detector) were used to analyze the components of the hydrocarbon from the collected pyrolysis gas product. The oven temperature was set at 60 °C, and the injector at 100 °C, detector at 150 °C. Each sample gas was detected three times to ensure repetition.

RESULTS AND DISCUSSIONS

1. Comparison of the TG Curves of Longkou Lignite Pyrolysis in Two Kinds of Atmosphere

The weight loss (TG curves) of Longkou lignite pyrolyzed under nitrogen and methane ambience with three different heating rates are shown as Fig. 3(a), (b).

It is shown in the Fig. 3 that the TG-DTG curves of lignite pyrolyzed in N_2 and CH_4 ambience with heating rate of 10 °C/min and 20 °C/min have similar characteristics. Under N_2 atmosphere, weight loss appeared at 200 °C and then the TG curves dropped continuously; the DTG curves also decreased at the same time. The rate of weight loss reached a maximum at 465 °C. Comparably, under CH_4 atmosphere, weight loss appeared at 300 °C. The TG curves were almost superposed in nitrogen and methane ambience before 360 °C. It indicates that methane cannot promote the pyrolysis of lignite below a temperature of 360 °C. However, the rate of coal weight loss in methane ambience is obviously higher than in nitrogen ambience from 360 °C to 540 °C. This phenomenon indicates that methane promoted the pyrolysis of coal in the temperature range. Then the TG curves of coal pyrolysis in methane begin to climb up above

750 ºC and the weight increase appears, which proves that there is reciprocity between coal and methane. This phenomenon may be accounted in terms of the carbon deposition occurring during methane pyrolysis. According to the blank TG curve of methane, it cannot pyrolyze below 950 ºC without coal, which demonstrates that coal promotes the pyrolysis of methane. Egiebor and Gray think that coal can activate the methane and promote its pyrolysis at lower temperature to give methyl, dimethyl products and hydrogen free radical, which promotes coal pyrolysis in reverse [5]. Therefore, the rate of coal weight loss in CH_4 atmosphere is higher than in N_2, and the TG curves of coal pyrolysis are more gradient than under N_2 ambience. In conclusion, methane can promote the pyrolysis of coal and the coal can also improve the pyrolysis of methane in reverse.

2. The Characteristics of Hydrocarbon Released from Longkou Lignite Pyrolysis in Different Concentration of Methane Ambience

Fig. 4(a) shows that there is an obvious peak of decline about methane concentration in the temperature range from 350 ºC to 650 ºC, which indicates that methane pyrolyzed in this range. The con-

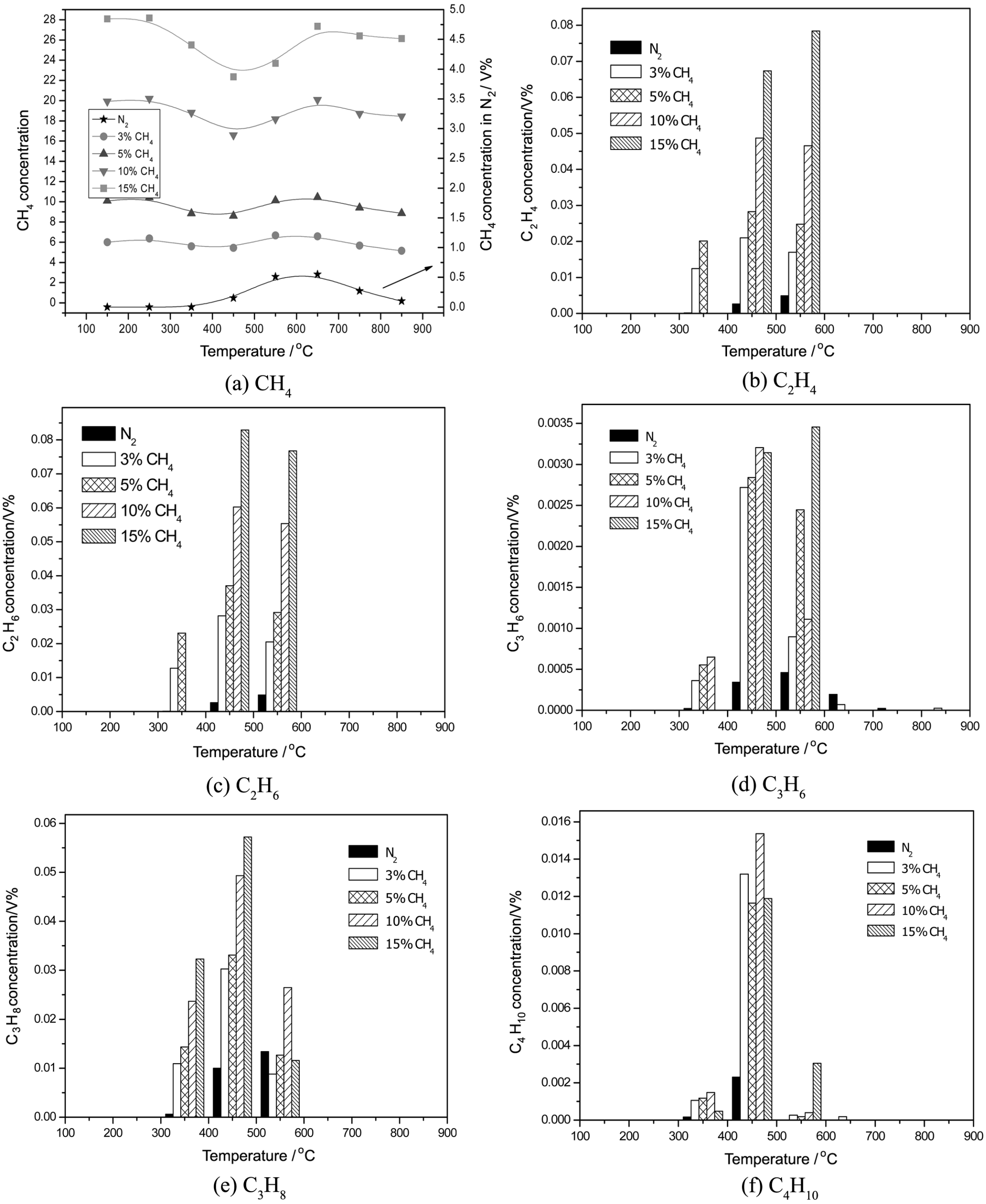


Fig. 4. Variable concentration of hydrocarbon released from lignite pyrolysis in different concentration of methane ambience.

centration of methane began to decrease again above 700 °C. It can be seen from the TG curves that the phenomenon is due to carbon release from methane pyrolysis at 700 °C. The peak of decline is more obviously with the increase of methane concentration, which magnifies the pyrolysis of methane within the range. So we can clearly see that the pyrolysis reactions are affected by methane concentration. But methane cannot pyrolyze below 950 °C without coal. According to the results of thermogravimetric experiment and studying the results of predecessors, abundant activated free radicals were released from the coal pyrolysis and some of them can promote methane pyrolysis. It can be seen from Fig. 4(a) that the temperature range of activated free radical release should from 350 °C to 650 °C. This proved the result that methane can promote coal pyrolysis within the temperature range in our thermogravimetric experiment.

However, we can see clearly from this figure that the concentration of methane from coal pyrolysis in N_2 atmosphere is much lower than in different concentration of CH_4 atmosphere. The methane is absolutely from coal pyrolysis in N_2 atmosphere and its concentration continuously increased and reached the peak at around 600 °C. To sum up, coal pyrolysis is affected greatly by methane.

As is shown in Fig. 4(b)-(f), the C_2H_4, C_2H_6, C_3H_6, and C_4H_{10} except C_3H_8 were detected at the temperature range 400-600 °C when the concentration of methane is high (10% or 15%) and the releasing is more than that in low methane concentration. All the hydrocarbon amount reached a maximum at 400-500 °C under different methane concentration ambience. In Fig. 4(c) and 4(e), we can see that the characteristics of released C_2H_6 and C_3H_8 are similar and they show good regulation for releasing. With the increase of methane concentration the amounts of releasing increase. And in other figures, the amount of hydrocarbon reaches a maximum in 10% concentration of methane ambience and declines a little in 15%. In N_2 atmosphere, the amount of each hydrocarbon released from coal reached maximum also at around 500 °C. Compared with different concentration of CH_4 atmosphere, each hydrocarbon component from coal in N_2 atmosphere is much less, as is shown in Fig. 4(b)-4(f). This obviously proves that methane can promote the release of hydrocarbon from coal.

In conclusion, the hydrocarbon began to release from lignite pyrolysis at around 350 °C, which indicates that the volatile is released from lignite pyrolysis at the temperature and gives the activated free radicals to promote methane pyrolysis. The activated methyl given by methane pyrolysis can also promote coal pyrolysis [6]. The association reactions of free radicals (for example, $CH_3+H\rightarrow CH_4$, $CH_3+CH_3\rightarrow C_2H_6$, …) can be elementary bimolecular reactions [7]. Therefore, the hydrocarbon components released are the most drastic in the temperature range from 400 °C to 500 °C, in which the rate of coal weight loss in methane ambience is higher than in nitrogen and a peak appears in the thermogravimetric experiment. The methane concentration declined and other hydrocarbon obviously released in this temperature range, which proves that methane reacted in the coal pyrolysis reaction and produced a mass of light hydrocarbon such as C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10}. These hydrocarbons may be from methane pyrolysis or coal pyrolysis or reciprocity between them.

CONCLUSION

1. In the temperature range from 360 °C to 540 °C, the rate of coal weight loss in methane ambience is obviously higher than in nitrogen ambience, which indicates that methane promoted the pyrolysis of coal within the temperature scope.

2. Above 750 °C, the TG curves of coal pyrolysis in methane begAn to climb up and the weight increase appeared, which proves that there is reciprocity between coal and methane; the phenomenon may be accounted for in terms of carbon deposition occurring during methane pyrolysis. Methane cannot pyrolyze below 950 °C without coal, which demonstrates that coal promoted the pyrolysis of methane.

3. Methane pyrolyzed in 350-650 °C with coal existed and the concentration declined again above 700 °C owing to carbon beginning to release from methane. This phenomenon is more obvious as the methane concentration increased.

4. C_2H_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10} was released intensively during 400 °C to 500 °C, and the concentration of light hydrocarbon increased with the methane concentration increasing.

In a word, methane influenced coal pyrolysis and hydrocarbon releasing. So there is reciprocity between coal and methane and the characteristic of coal pyrolysis varies as the concentration of methane changes.

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