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Co-pyrolysis of Pyridine and Pyrrole as Nitrogenous Compounds Model of Coal

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Nitrogen in coal mainly exists in the form of pyrrolic nitrogen and pyridinic nitrogen, in this work, pyridine and pyrrole has been chosen as the nitrogenous model compound to investigate the transformation of nitrogen in coal during pyrolysis and combustion. The pyrolysis of mixture of pyridine and pyrrole is performed at 873-1473 K in a flow reactor and the products are analyzed by FTIR combined with GC. Results show that the thermal stabilization of pyridine is better than pyrrole and pyridine produces more H_2 but less HCN. HCN yield of co-pyrolysis is lower than the separate pyrolysis of both pyridine and pyrrole. Co-pyrolysis releases more HCN with the increase of pyridine content at 1373 K, in contrast to 1073 K. The change of H_2 is similar to HCN as the temperature and mixing ratio change and CH_4 is detected with low yield.

Key Words: HCN, H_2, FT-IR, Pyridine, Pyrrole.

INTRODUCTION

The nitrogen oxides produced during coal combustion not only generate acid rain and destroy the ozonosphere, but also form photochemical smog as well[1]. There are four forms of nitrogen in coal to be determined by the XPS and XANES methods, mainly including pyridine nitrogen, pyrrole nitrogen, protonized pyridine and nitrogen oxides[2,3].

Many scholars suggest that the model compounds should be used to replace the coal to research the transformation mechanisms of nitrogen in coal. The main nitrogenous substance obtained by Zhiheng[4] from pyroysis of cellulose and phenol was mainly HCN. The main nitrogenous products in pyrolysis of pyrrole obtained by Lifshitz[5] were pyrrole allotropes, HCN and propane transformed. The nitrogenous products contain mainly HCN obtained by Mackie[6] when pyrogenating pyrrole at high temperatures, with other pyrolitic products covering acetylene, methane and hydrogen and the corresponding pyrolytic mechanisms were also presented.

Liu *et al.*[7] measured the content of various type of nitrogen element in the Yibin raw coal, Tongchuan raw coal and coke. The research shows that the rate of the content of the nitrogen of the Yibin raw coal in the pyrrole and the pyridine form is

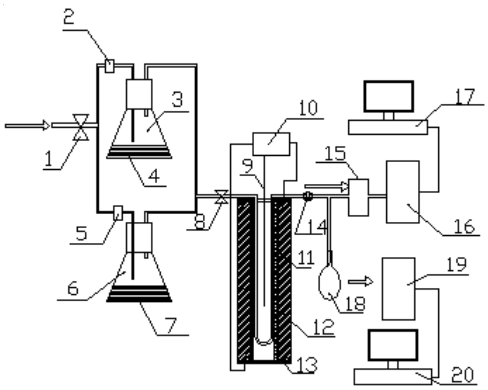
2:1 and for the Tongchuan raw coal is 1:1. Nitrogen is present in the pyrrole form in the high-temperature coke. In the present studies, the content of pyridine is defined as follows:

$$\text{Pyridine} = \frac{\text{Mass of pyridine}}{\text{Mass of pyridine} + \text{Mass of pyrrole}} \times 100\ \% \qquad (1)$$

According to the content of the pyridine nitrogen and pyrrole nitrogen of the Yibin raw coal, Tongchuan raw coal and coke mentioned above, we conducted proportional pyrolysis in the experiment by choosing pyridine = 0, 28.6, 50.0, 66.7 and 100 %. The influence of temperature and mixing rate on the pyrolysis products is discussed.

EXPERIMENTAL

As seen from Fig. 1, high-purity argon, which was used as the gas carrier, blew over the liquid surface in the conic bottle to make the model compounds speed up evaporation and carry the vapour into the reactor. The reactor is a U-type quartz vessel 20 mm in inner diameter, 2 mm in thickness and 450 mm in one-sided tube length. The model compound entered from the left branch pipe and the pyrolytic products flew out of the right branch tube. For the measuring of temperature and controlling system, a platinum rhodium-platinum thermocouple was used to measure the temperature, a silicon carbide tube heater was employed as the heating element and a smart temperature control meter was used as the temperature control instrument.



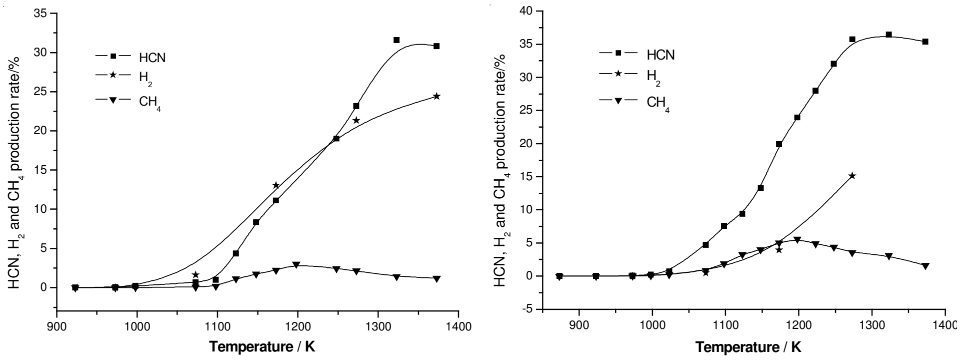
1. Relief valve; 2. A rotameter; 3. Feeder for pyridine; 4. Pyridine; 5. B rotameter; 6. Feeder for pyrrole; 7. Pyrrole; 8. Pressure stabilization valve; 9. Thermocouple; 10. Temperature controller; 11. Corundum tube; 12. SiC tube heater; 13. Heating electrode; 14. Filtering absorber; 15. Dilution buffering bottle; 16. Gas analyzer; 17. Gas analyzer data gathering PC; 18. Sampling device; 19. Gas chromatograph; 20. Gas chromatograph data gathering PC

Fig. 1. Schematic diagram of experimental system

The concentration of HCN, NH_3 and CH_4 in flue gas was detected on-line by a Helsinki made DX-4000 FT-IR gas analyzer, which has a 1.07 L gas analysis cell with a path of 5 m, resolution of 8 cm^{-1}, response time < 120 s, wave-number range of 4200-900 cm^{-1} and scan frequency of 10 spectra/s. The lowest detectable concentration was 1 ppm and the estimated uncertainty limits of measurements were estimated to be within ± 2 %. A thermal conductivity detector SP-2100 GC, which has a stationary phase of 5A molecule sieve, carrier gas of argon, column of 4 mm × 5 m and column temperature of 341 K was used to quantify the concentration of H_2 and N_2.

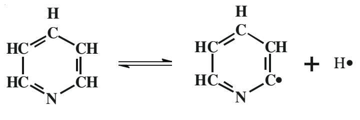
RESULTS AND DISCUSSION

Separate pyrolysis of pyridine and pyrrole: It can be seen from Fig. 2 that the temperature at which pyrrole begins to produce HCN in large quantity is rather low *i.e.*, around 1048 K. The temperature at which pyridine begins to produce HCN in large quantity is up to 1098 K. The H_2 production rate of pyrrole is much lower than that of pyridine while the temperature at which pyrrole begins to produce HCN is higher than that of pyridine. During the pyrolysis of pyridine, H_2 begins to produce in large quantity earlier than HCN at a lower temperature, whereas during the pyrolysis of pyrrole, HCN begins to produce in large quantity earlier than H_2 at a lower temperature. This suggests that pyridine takes a pyrolytic ring-opening form different from pyrrole. Pyridine is earlier to have the reaction to produce the pyridine free radical and hydrogen activated molecule as shown in the following conversions:



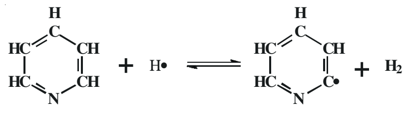
(a) Pyridine (b) Pyrrole

Fig. 2. Influence of temperature on products of separate pyrolysis



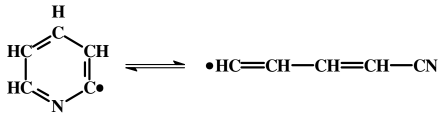
(2)

The unstable activated hydrogen molecule will continue to take away the H_2 molecule at the α-position of pyridine:



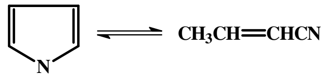
(3)

With the rise of temperature, the pyridine free radical implements the cycloreversion to change itself to the chain form:

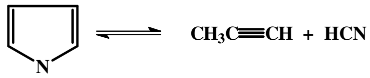


(4)

The pyrolysis of pyrrole differs in that it realizes direct ring-opening without passing through the free radical reaction:



(5)



(6)

It is obvious that the variance of the molecular structure of pyridine and pyrrole results in great difference in their pyrolysis ring-opening form.

Comparison of HCN formation between mixed pyrolysis and separate pyrolysis, it is clear from Fig. 3 that the tendency of the production rate of HCN changing with the temperature in the mixed pyrolysis and separate pyrolysis coincides. However, at high temperatures, the amount of HCN produced finally during the separate pyrolysis is greater than that during the mixed pyrolysis.

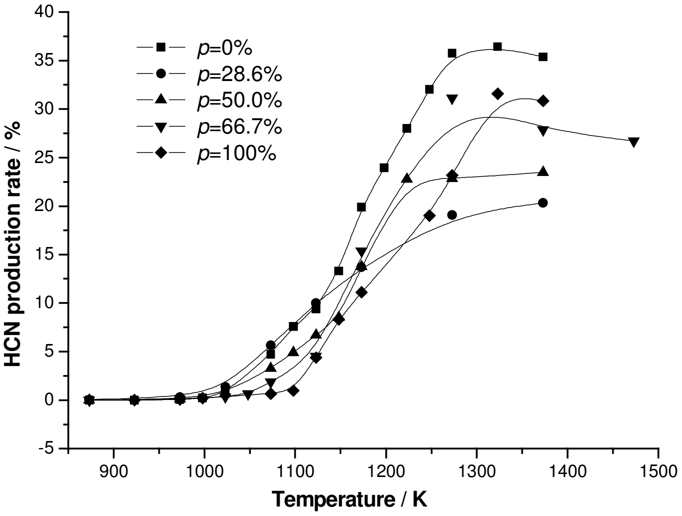
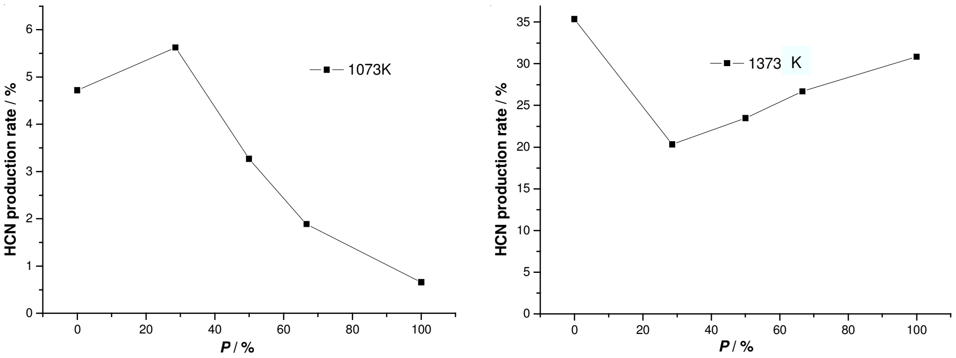


Fig. 3. Influence of temperature and pyridine content on the mixed pyrolytic product HCN

In order to compare the relationship between the HCN production rate and the pyridine content, two temperature levels of 1073 K and 1373 K are taken as shown in Fig. 4. At 1073 K, the HCN production rate decreases with the increase in the pyridine content. This is because at this time, HCN stems mainly from the pyrrole pyrolysis. The HCN production rate in the pyrolysis of pyrrole is 5 %, while HCN production rate in the pyridine pyrolysis is merely 0.5 %. This denotes that the thermal stability of pyridine is higher than that of pyrrole. This agrees with the result where the HyperChem program was used to construct a molecule model and the density functional method was employed to carry out the theoretical computation of the quantum chemistry[7]. When the pyridine content was 28.6 %, the HCN production rate was slightly greater than that of the pure pyrolytic pyrrole. It is assumed that pyridine plays an intensifying role in the production of pyrrole. It is clear from Fig. 2 that at 1073 K pyridine has produced H_2, but pyrrole dose not. A massive amount of research has manifested that the pyridine and pyrrole pyrolysis is a series of free radical reactions. As a result, at this temperature, the pyridine which does not produce HCN, but produce more H activated molecules to provide a more active environment for the pyrrole pyrolysis to produce more HCN.

Fig. 5 shows the relationship between the H_2 production rate and the pyridine contents at 1073 K, 1173 K and 1273 K.



(a) 1073 K (b) 1373 K

Fig. 4. Relationship between HCN production rate and pyridine at different temperatures

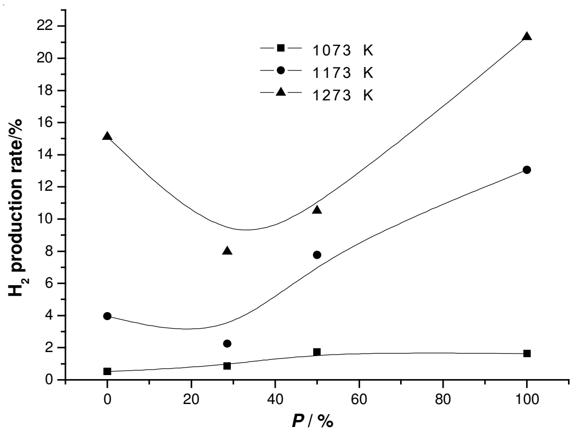


Fig. 5. Relationship between H_2 production rate and pyridine at different temperatures

At 1373 K, the HCN production rate during the separate pyrolysis of pyridine is slightly lower than that of pyrrole. With the increase in the pyrrole content, the inhibition effect of pyridine on pyrrole will get more intensive and simultaneously, at high temperatures, pyridine has already begun to produce a great amount of HCN so that pyridine dominates the changing tendency of HCN and the HCN production rate grows with the increase of the pyridine content.

Comparison between the H_2 and HCN production rates: Fig. 6 indicates that during the pyrolysis course, the tendency of the production rate of H_2 is similar to that of HCN. It is inferred that the production of HCN is related to H_2. Fig. 7

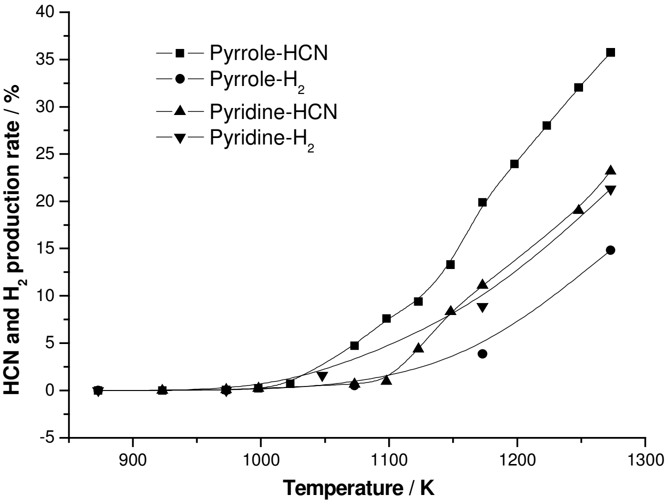


Fig. 6. Comparison of the distribution of HCN and H_2 relative to temperature

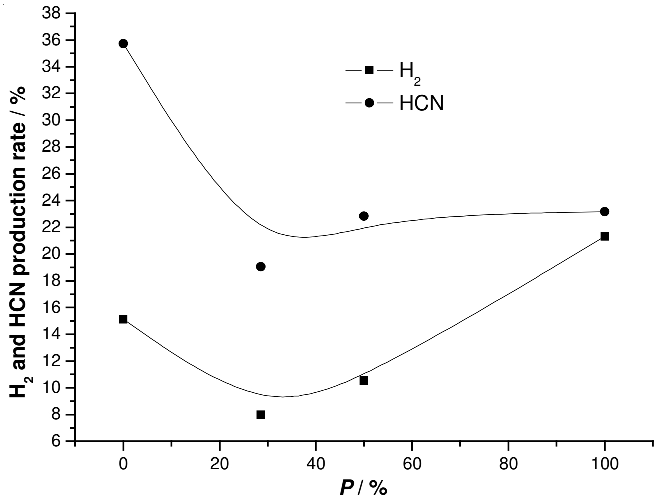


Fig. 7. Comparison of distribution of the production rate of HCN and H_2 relative to pyridine at 1373 K

further shows that at 1373 K, the tendency of the production rate of HCN and H_2 is more similar when coupled with the change of mixing proportion. H_2 affects the generation of HCN. Since the free radical reaction is adulterated in the pyrolysis course of two substances, it is easy for the H free radical to take away the H from other component to produce H_2, as an exceptionally unstable component. The massive existence of H_2 will undoubtedly provide an extremely active environment for the pyrolysis, thus enabling the reaction to take place more intensively and thoroughly and determining the production rate of HCN. The change of HCN and H_2 with the variance of the pyridine content has a similar tendency.

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