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ORIGINAL RESEARCH ARTICLE

Effects of atmosphere and post catalyst on pyrolysis characteristics of Pingshuo bituminous coal

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ABSTRACT

In order to lighten the tar from coal pyrolysis, the effects of N_2, CH_4 and H_2 atmosphere on the pyrolysis characteristics of Pingshuo bituminous coal were investigated in a small fluidized bed, and Ni-based catalyst was placed downstream of coal pyrolysis to catalyze the upgrading of tar. The results show that both H_2 and CH_4 atmosphere can improve the conversion of coal pyrolysis and improve the yield of pyrolysis tar. Compared with CH_4 atmosphere, the post placed Ni-based catalyst in CH_4 atmosphere can increase the tar yield by 10%, increase the gas yield and H_2 yield, and transform the pyrolysis tar to the light direction. Through simulated distillation and GC-MS analysis, compared with N_2 atmosphere, CH_4, H_2 atmosphere and CH_4 + Ni increased the relative contents of naphtha, phenol oil, naphthalene oil, wash oil and anthracene oil, and the increase showed that CH_4 + Ni > H_2 > CH_4, while the asphalt content decreased. Compared with CH_4, the relative contents of aromatic hydrocarbons and aliphatic hydrocarbons increased significantly under CH_4 + Ni.

Keywords: Pyrolysis; Tar Lightening; Fluidized Bed; Post Catalyst

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1. Introduction

Poly-generation technology based on pyrolysis can obtain high value-added products such as semi-coke, gas and tar[1], which can not only alleviate the environmental problems caused by energy utilization from the source, but also create higher energy economic benefits. In recent years, researchers at home and abroad have paid extensive attention to the effects of atmosphere and catalyst on coal pyrolysis characteristics. Gao *et al.*[2] studied coal hydropyrolysis in a falling fixed bed at atmospheric pressure, the results show that the yield of tar from hydrotreating at 800 ℃ is 30% higher than that in N_2 atmosphere. Hydrotreating can promote the lightening of tar. Chen[3] studied the hydropyrolysis of lignite in a fixed bed. The results show that with the increase of H_2 concentration, the yield of tar increases monotonously, and the aromatic hydrocarbons and phenolic compounds in tar also increase[4]. However, the high cost of H_2 restricts the development of hydro pyrolysis[5,6], CH_4 with high hydrogen carbon ratio and relatively low cost will replace H_2 in coal pyrolysis technology[4]. Coal pyrolysis in fixed bed CH_4 atmosphere shows CH_4 atmosphere is equivalent to inert atmosphere at low temperature which has little effect on the yield of tar. Yan[7] found that the tar yield can be improved under the low temperature of small fluidized bed CH_4, and the tar yield will be flluidized bed CH_4, and the tar yield will be further improved under the high temperature due to the free radicals and hydrogen produced by the decomposition of methane. CH_4 can improve the yield of tar, but the effect is limited. The catalytic activation of methane to improve the yield of tar has been widely concerned. The influence of different catalyst and catalyst arrangement on tar yield was investigated in fixed bed by Zhao[8]. It was found that Mo/HZSM-5 and Ni/Al_2O_3 could increase tar at 600 °C by 17.5%, and the content of light components in tar is more than 90%. Wang *et al.*[9] improved tar yield by combining in-situ catalytic cracking of coal pyrolysis tar with methane in a fixed bed, and the average molecular weight of tar decreased. Compared with 5% Co/Al_2O_3 and 5% Fe/Al_2O_3, 5% Ni/Al_2O_3 obtained light tar with higher content and yield. Li[10] found that adding pre-Mo/HZSM-5 in CH_4 atmosphere can greatly improve the tar yield, and the pre-catalyst has better effect than the mixing of coal and catalyst. Yan[7] found that the addition of Ni-based catalyst under CH_4 + N_2 atmosphere increased the tar yield at 600 °C by 40% and the aromatic hydrocarbons content by 16% compared with no catalyst added.

Based on the above research results, CH_4, H_2 atmosphere and catalyst can effectively improve the yield and quality of coal pyrolysis tar, and the separation of coal and catalyst is better. However, nowadays, most of the catalytic activation of methane is carried out in fixed bed, and less research is involved in small fluidized bed which is closer to industrial application. Therefore, this study investigated the effects of N_2, CH_4 and H_2 atmosphere on the pyrolysis characteristics of Pingshuo bituminous coal in a small fluidized bed, and placed Ni-based catalyst on the downstream of coal pyrolysis to achieve the goal of catalytic upgrading of coal pyrolysis gas-phase tar before condensation.

2. Experimental part

2.1 Preparation of coal sample and catalyst

Shanxi Pingshuo bituminous coal was selected as the experimental coal, and the raw coal was crushed and screened to obtain a particle size of 1.25–2 mm coal samples. Before the experiment, the coal sample was dried in a blast drying oven at 105 °C for 6 hours, sealed and stored for use. The fluidizing medium of fluidized bed is 0.25–0.35 mm quartz sand. See **Table 1** for industrial analysis and elemental analysis of experimental coal samples.

Table 1. Industrial analysis and elemental analysis of Pingshuo bituminous coal

Industrial analysis w_{ad}/%				**Elemental analysis w_{ad}/%**				
M	A	V	FC	C	H	N	S	O*
1.20	39.08	25.31	34.41	42.49	2.16	0.94	2.47	11.66

*Obtained by subtraction

The catalyst Ni/Al_2O_3 is prepared by equal volume impregnation[11]. It is impregnated with Ni $(NO_3)_2 \cdot 6H_2O$ salt solution for 12 hours, dried at 105 °C for 6 hours, roasted at 550 °C for 6 hours, sealed and stored for later use after reduction, and the Ni load is 5% (mass fraction).

2.2 Experimental method

The small-scale fluidized bed pyrolysis experimental system used in the experiment is shown in **Figure 1**. The experimental system is mainly composed of a gas supply system, a preheating section, a reaction section, a heat preservation section (catalyst placement section), and a product collection device. The inner diameter of the preheating section is 20 mm, and the length is 3.5 m, the inner diameter of the reaction section is 50 mm, and the length is 1.2 m, heated by silicon carbide rods arranged uniformly and graded, the temperature can reach 1,000 °C, and the insulation section is heated by resistance wire. The liquid collection device is composed of two-stage serial serpentine tubes (placed in a constant temperature and low temperature tank at -10 °C), filters and three-stage parallel glass fiber filter cartridges to ensure complete collection of tar and water.

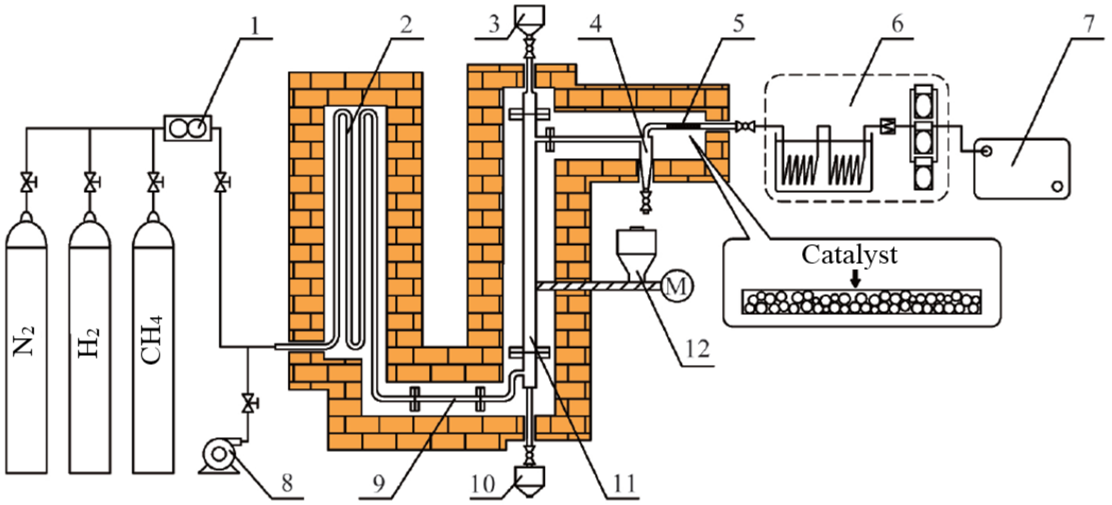

Figure 1. Experimental system of small fluidized bed pyrolysis.
1–mass flowmeter; 2–preheating section; 3–upper hopper; 4–cyclone separator; 5–catalyst; 6–liquid collection device; 7–air bag; 8–air pump; 9–horizontal section; 10–lower hopper; 11–reaction section; 12–screw feeder.

Before the experiment, 550 g quartz sand was fed from the upper hopper as bed material. Set the heating program and wait for the fluidized bed furnace body to rise temperature, during which a small amount of N_2 is introduced to ensure safe operation. When the temperature of the reaction section rises to the pyrolysis temperature, adjust the fluidization gas volume to 25 L/min. The fluidization gas is N_2, and the mixed volume ratio is 60% N_2 + 40% CH_4 and 60% N_2 + 40% H_2. When the atmosphere is completely replaced with the pyrolysis atmosphere set in the experiment, slowly feed 30 g of coal sample from the upper hopper, immediately open 120 L aluminum foil air bag to collect the gas. The pyrolysis tar and water are fully condensed through the liquid collection device, and the pyrolysis time is 3 min. After the reaction, open the lower hopper to collect the semi-coke and bed material, remove the hopper and seal it for storage to prevent the high-temperature oxidation of the semi-coke. After it is naturally cooled to room temperature, sieved to obtain the quality of the semi-coke. The tar and water are washed repeatedly with analytical pure acetone solution, and sealed and stored after filtering the fly ash. The quality of tar and water is obtained by the subtraction method from the quality of the liquid collection device before and after the reaction. The post catalyst is placed behind the cyclone separator, the temperature of the catalytic section is set to 500 °C, and the amount of catalyst is 12 g.

2.3 Calculation, measurement and analysis of pyrolysis product yield

The water content of the tar was measured with ZDJ-2S card type micro moisture tester to calculate the mass of water and tar. The volume of pyrolysis gas is obtained according to the difference between the measured volume of gas meter and the volume of carrier gas. The yield of pyrolysis products is calculated by the following formula:

$$Y_{\text{char}} = \frac{W_{\text{char}} - W \times A}{W \times (1 - A - M)} \times 100\% \tag{1}$$

$$Y_{tar} = \frac{W_{tar}}{W \times (1 - A - M)} \times 100\% \tag{2}$$

$$Y_{water} = \frac{W_{water} - W \times M}{W \times (1 - A - M)} \times 100\% \tag{3}$$

$$Y_{gas} = \frac{V_{gas}}{W \times (1 - A - M)} \times 100\% \tag{4}$$

In the equation: Y_{char}, Y_{tar}, Y_{water} and Y_{gas} are the yields of semi-coke, tar, water and gas respectively (calculated on dry ash free basis); W_{char}, W_{tar} and W_{water} are the quality of semi-coke, tar and water respectively; V_{gas} is the volume of gas; W is the quality of pyrolysis coal; *A* and *M* are the ash and moisture content of coal sample (calculated on air drying basis).

The gas components are detected by Agilent 7890A, and standard gas is used for calibration before detection. The gas components CH_4, C_2–C_3 (the sum of C_2H_4, C_2H_6, C_3H_6 and C_3H_8), CO, CO_2 and H_2 were obtained and the yield of the above components are calculated.

After the moisture content of the tar solution is measured, the excess anhydrous sodium sulfate is used to remove the moisture, and then the tar sample is obtained by distillation with a rotary distiller for 6 hours. The distillation temperature is 62 °C and the rotating speed is 20 r/min. The tar components are analyzed by GC-MS with GC/MS-QP2010SE. The tar sample is diluted to 5% with analytical pure CH_2Cl_2 and then injected. The temperature of the injection port is 300 °C. The chromatographic column model is SH-Rxi-5Sil MS and its specification is 30 m × 0.25 mm × 0.25 μm. GC temperature rise procedure: column temperature was kept at 60 °C, maintained for 2 min; then raise the temperature to 180 °C at the heating rate of 4 °C/min for 2 minutes, and finally raise the temperature to 300 °C at the heating rate of 10 °C/min for 10 minutes. The tar fraction is obtained by simulated distillation of gas chromatography Agilent 7890A, and the specification of packed column is 1/8 inch × 0.5 m, the tar sample is diluted to 5% with analytical pure CS_2 and then injected. The temperature rise procedure of GC is: the initial temperature is 35 °C and maintained at 35 ℃ for 0.5 min; rise to 350 °C at the heating rate of 10 °C/min for 1 min, then rise to 400 °C at the heating rate of 5 °C/min for 10 min. During determination, H_2 (40 mL/min) and air (400 mL/min) are combustion gas and N_2 (25 ml/min) is carrier gas.

3. Results and discussion

In this paper, the pyrolysis product yield, gas component yield, tar component and fraction distribution characteristics of Pingshuo bituminous coal under different pyrolysis temperatures (500 °C, 600 °C, 700 °C, 800 °C), different pyrolysis atmospheres (N_2, 60% N_2 + 40% CH_4, 60% N_2 + 40% H_2, abbreviated as N_2, CH_4, H_2 for convenience) and post catalyst Ni/Al_2O_3 were investigated in a small fluidized bed.

3.1 Effect of atmosphere on the yield of coal pyrolysis products

Figure 2 shows the yield law of coal pyrolysis products under different pyrolysis atmospheres and different pyrolysis temperatures. The mass recovery of each experiment is more than 94%, and the experiment has good repeatability.

Figure 2(a) shows the effects of different atmospheres on the yield of semi-coke from coal fluidized bed pyrolysis. Under the three atmospheres, the yield of coal pyrolysis semi-coke decreased gradually with the increase of pyrolysis temperature. Compared with N_2 atmosphere, the yield of semi-coke in H_2 atmosphere decreases, and the trend is basically the same as that in N_2 atmosphere. In the process of coal pyrolysis, the activated hydrogen free radicals provided by the H_2 atmosphere combine with the fragment free radicals generated by the breakage of chemical bonds in the coal, reducing the degree of polycondensation between fragments., which effectively improves the coal pyrolysis conversion and promotes the release of volatile matter. Compared with N_2, CH_4 atmosphere reduces the yield of semi-coke in the low temperature section lower than 600 °C, indicating that CH_4 atmosphere promotes the coal pyrolysis reaction at low temperature. However, the degree of CH_4 atmosphere promoting coal pyrolysis at low temperature is not as good as that of H_2 atmosphere, which indicates that the nature of CH_4 at low temperature is relatively stable and the amount of activated free radicals provided is small. While in the high temperature section above 700 °C, the CH_4 atmosphere increases the yield of semi-coke. Because there are two competitive reactions of CH_4 atmosphere on coal pyrolysis: on the one hand, the free radicals generated by CH_4 decomposition stabilize the molecular fragments generated by coal pyrolysis and inhibit the polycondensation reaction of fragments, so as to improve the conversion of coal; on the other hand, decomposition of methane occurs at high temperature $CH_4 \rightarrow C + 2H_2$, and the pyrolysis carbon deposition leads to an increase in the semi-coke yield, while inhibiting the precipitation of volatiles in the semi-coke. This confirmed that the increase in pyrolysis semi-coke yield at high temperature is mainly caused by the carbon deposition of methane cracking at high temperature.

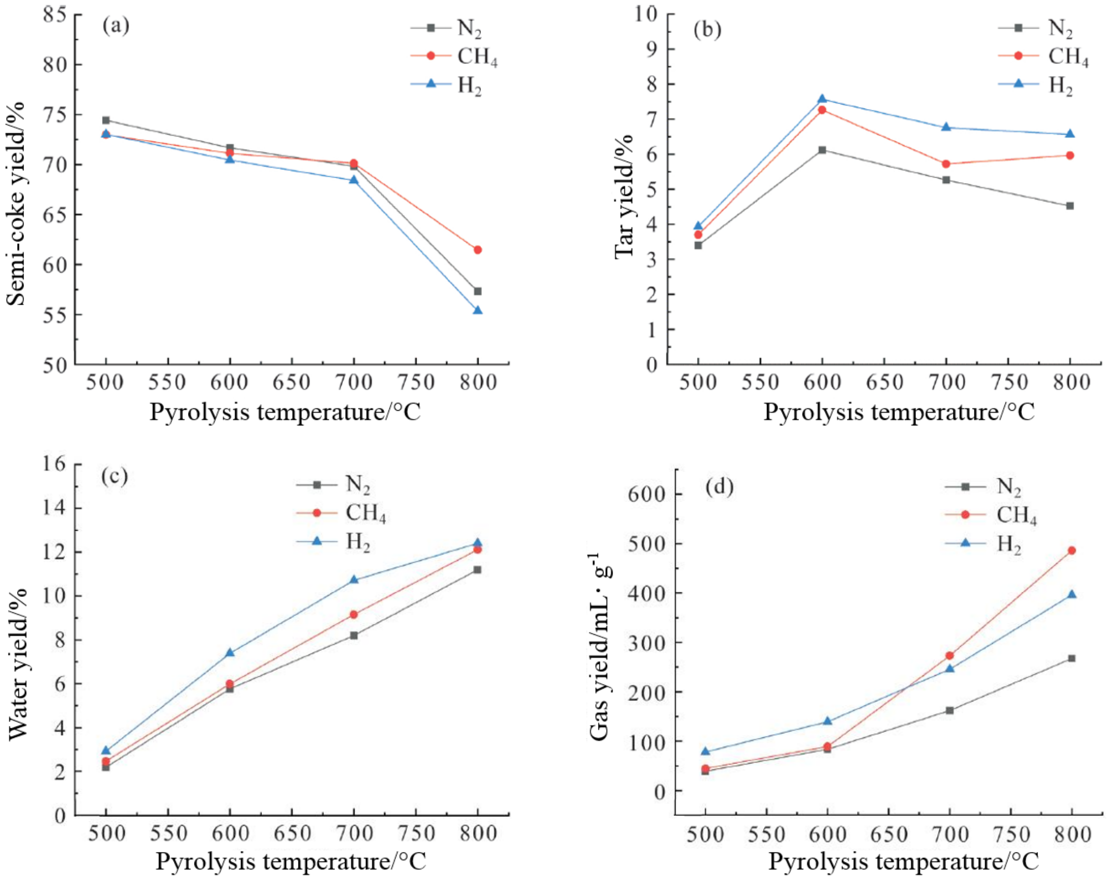

Figure 2. Yield of coal pyrolysis products under different atmospheres.

Figure 2(b) shows the effects of different atmospheres on the yield of tar from coal fluidized bed pyrolysis. It can be seen that the yield of pyrolysis tar first increases and then decreases with the increase of pyrolysis temperature in N_2 and H_2 atmosphere, and reaches the maximum at 600 ℃. Under CH_4 atmosphere, the tar below 700 ℃ meets the trend of first increasing and then decreasing, while the tar yield is higher than 700 ℃ at 800 ℃. This is related to the previous H_2 production from methane cracking at high temperature. CH_4 cracking at 800 ℃ produces a large amount of H_2, so the tar yield is further improved compared with 700 ℃. Compared with N_2 atmosphere, CH_4 and H_2 atmosphere can promote the increase of tar yield, and the promotion effect of H_2 is more obvious. This is because these two gases produce a large number of free radicals, which stabilize the macromolecular groups produced by coal pyrolysis, and H_2 atmosphere has a stronger ability to provide hydrogen free radicals.

Figure 2(c) shows the effect of different atmospheres on the yield of pyrolysis water in fluidized bed. Under the three atmospheres, the yield of pyrolysis water increases gradually with the increase of pyrolysis temperature, and the increasing trend in the high temperature section slows down. This is because more hydrogen radicals are produced at high temperature and the probability of reacting with O increases. Compared with N_2 atmosphere, H_2 atmosphere and CH_4 atmosphere promote the formation of pyrolysis water, and the yield of water in H_2 atmosphere is higher. This is because hydrogen free radicals combine with hydroxyl groups produced by coal pyrolysis to produce water. The number of hydrogen free radicals is the largest in H_2 atmosphere, so the yield of aquatic products is the highest.

Figure 2(d) shows the effects of different atmospheres on the yield of coal pyrolysis gas in coal fluidized bed. Under the three atmospheres, the gas yield increases gradually with the increase of pyrolysis temperature. This is because at high temperature, the organic matter in coal decomposes more completely and the gas is released more thoroughly. The effect of pyrolysis temperature on gas yield is more significant than pyrolysis atmosphere. Compared with N_2 atmosphere, the gas yield in H_2 atmosphere is increased. Under CH_4 atmosphere, the increase of gas yield in low temperature section is not obvious, because CH_4 atmosphere is inert in low temperature section. The increase of gas yield in high temperature section is significant, which is mutually confirmed by the decomposition of methane to produce hydrogen at high temperature.

3.2 Effect of atmosphere on the yield of gas components

Figure 3 shows the effect of atmosphere on the yield of each component of pyrolysis gas in coal fluidized bed. Because the carrier gas flow required for fluidization in this experiment is much larger than the amount of gas generated by pyrolysis, considering the metering error, this paper will no longer investigate the gas yield in the pyrolysis gas with the same composition as the carrier gas. As can be seen from **Figures 3(a)–3(e)**, with the increase of pyrolysis temperature, the yields of various gases produced by pyrolysis in different atmospheres show an increasing trend.

It can be seen from **Figure 3(a)** that H_2 atmosphere can significantly promote the formation of CH_4 during coal pyrolysis. The formation of CH_4 mainly comes from the bond breaking of alkyl compounds during pyrolysis[14]. The hydrogen radicals provided by H_2 atmosphere can effectively stabilize the side chain groups such as methyl and methylene separated from the macromolecular network of coal, so as to promote the formation of CH_4. In the figure, when H_2 atmosphere increases from 700 ℃ to 800 ℃, the small decrease of CH_4 yield is the result of the increase of CH_4 cracking rate at high temperature.

Figure 3(b) shows that compared with N_2 atmosphere, CH_4 and H_2 atmosphere are conducive to the formation of C_2–C_3 gas. At high temperature, free radicals such as methyl and methylene produced by coal pyrolysis can be combined with free radicals provided by CH_4 or H_2 atmosphere to form stable small molecular hydrocarbons[15]. At low temperature, CH_4 and H_2 have similar promoting effects on the release of C_2–C_3. At high temperature, the ability of CH_4 atmosphere to produce living free radicals gradually increases, and the yield of C_2–C_3 is slightly higher than that of H_2 atmosphere.

Figure 3(c) and **Figure 3(d)** show the changes of CO and CO_2 yields under different atmospheres, respectively. In the process of coal pyrolysis, the production of CO comes from the decomposition of carbonyl group, CH_3O-, phenolic hydroxyl and oxygen-containing heterocycles, while CO_2 mainly comes from the decomposition of carboxyl, esters and inorganic carbonates[16]. It can be seen that the increase of temperature will promote the decomposition of these functional groups and make the precipitation of CO and CO_2 more thorough. The existence of activated free radicals in pyrolysis atmosphere can also promote the bond breaking of functional groups and the formation of stable compounds. The yield of CO in H_2 atmosphere is higher than that in N_2 atmosphere, the yield of CO_2 is lower than that in N_2 atmosphere, because the occurrence of reaction $H_2 + CO_2 \rightarrow H_2O + CO$ promotes the conversion of CO_2 to CO, resulting in a more significant increase in the yield of CO. CH_4 atmosphere at 600 ℃ and below has little effect on the yield of CO and CO_2 in pyrolysis gas; the precipitation of CO_2 was slightly inhibited above 700 ℃, while the yield of CO was between N_2 and H_2 atmosphere. It can be inferred that the activation and decomposition of CH_4 is mainly above 700 ℃, while the CH_4 gas itself in the low temperature section has no obvious effect on the reaction of functional groups in coal.

Figure 3(e) shows the variation of H_2 yield with pyrolysis temperature in N_2 and CH_4 atmosphere. Dehydropolycondensation of aromatic structure in coal under N_2 atmosphere is the main source of H_2 in pyrolysis gas[17]. With the increase of pyrolysis temperature, the H_2 yield increases gradually and slowly. Compared with N_2 atmosphere, H_2 yield in CH_4 atmosphere increased significantly with temperature. At 700 ℃ and above, the high temperature decomposition of CH_4 in the carrier gas becomes the main source of H_2.

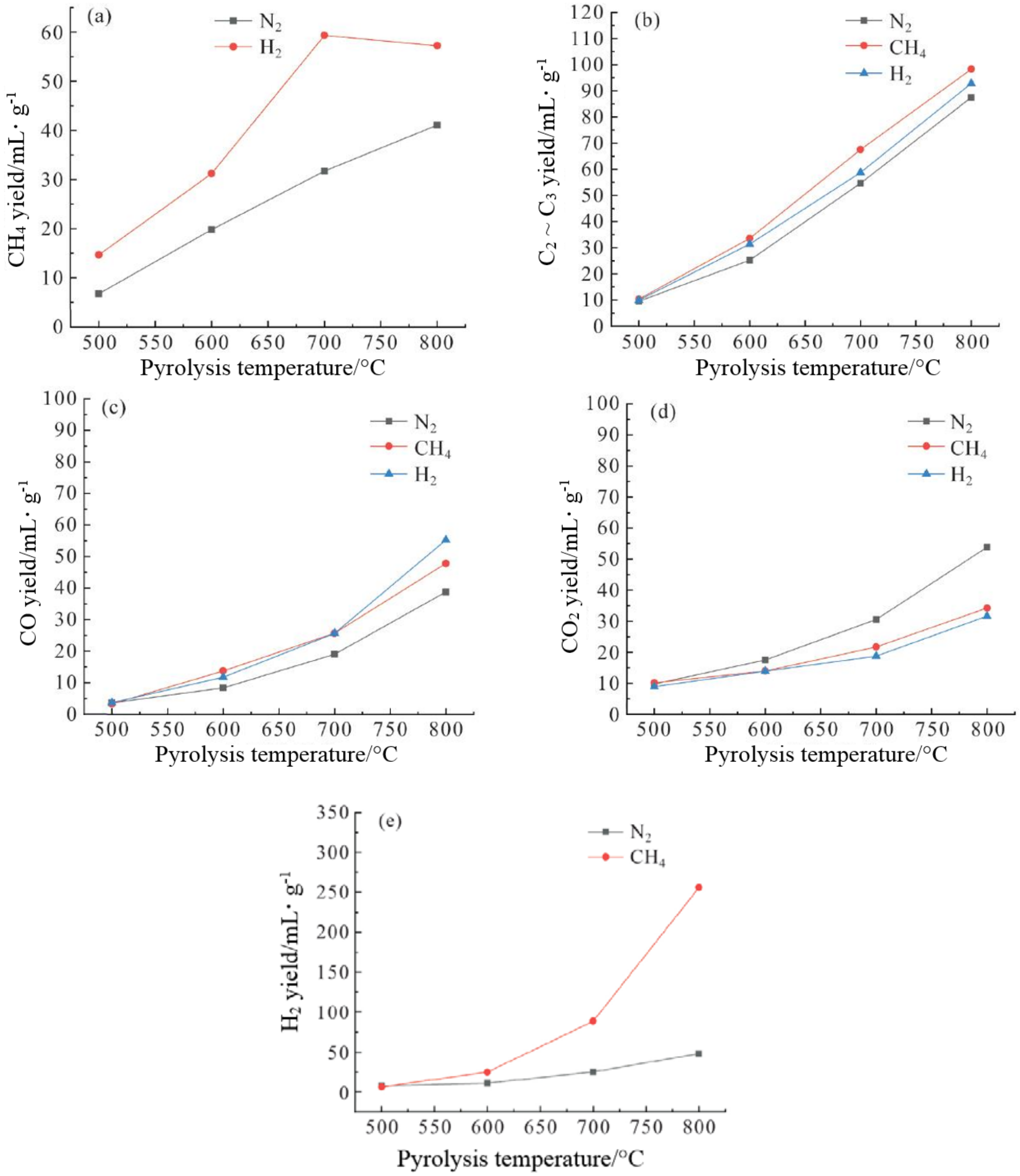

Figure 3. Yield of pyrolysis gas components under different atmospheres.

3.3 Effect of post catalyst on the yield of pyrolysis products

Figure 4 shows the effect of post catalyst Ni/Al_2O_3 on the yield of pyrolysis products. **Figure 4(a)** shows that under the action of post catalyst Ni/Al_2O_3, the yield of semi-coke is lower than that without catalyst. **Figures 4(b)–4(d)** show that the post Ni-based catalyst redistributes the gas-liquid products of coal pyrolysis. Under the condition of no catalyst, the yield increases by 600%, especially under the condition of no catalyst. The yield of aquatic products decreased and the yield of gas increased. The redistribution of the above product yields is attributed to the good catalytic effect of Ni catalyst on CH_4[18]. Due to the existence of Ni based catalyst, CH_4 atmosphere will produce more active radicals such as methyl, methylene and hydrogen radicals. These radicals will recombine the pyrolysis products after contacting with the volatile substances of coal pyrolysis, increasing the yield of tar and gas. As a result, coal pyrolysis is carried out more in the direction of volatilization analysis, resulting in a decrease in the yield of semi-coke.

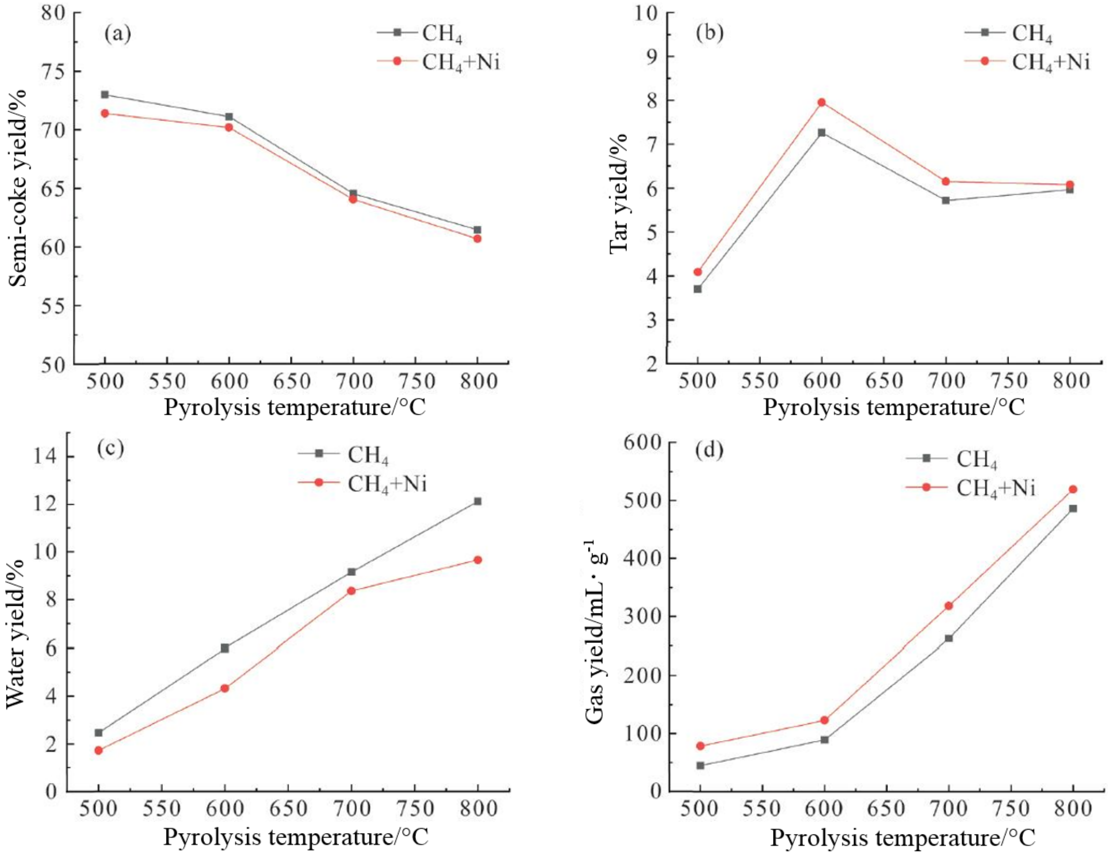

Figure 4. Effect of post catalyst on the yield of pyrolysis products.

Figure 5 shows the effect of post catalyst on H_2 yield. The results showed that Ni-based catalyst promoted H_2 precipitation at various pyrolysis temperatures, especially at 600 ℃ and 800 ℃. At 700 ℃, Ni-based catalyst has no obvious effect on H_2 yield.

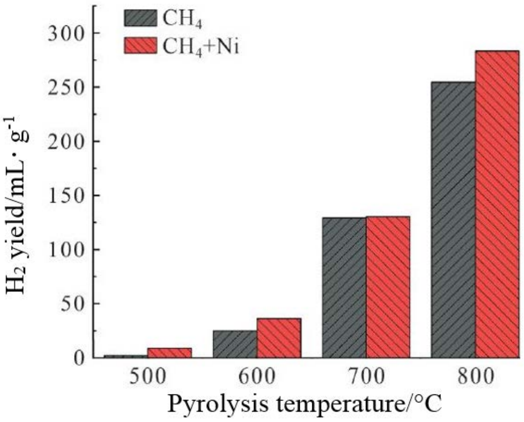

Figure 5. The effect of post catalyst on H_2 yield.

3.4 Influence of atmosphere and post catalyst on tar

Samples obtained under various working conditions shall be analyzed with simulated distillation and GC-MS. Tar samples of N_2, CH_4, H_2 and CH_4 + Ni at 600 ℃ were analyzed as representative data. According to ASTM D2887 method, tar is divided into naphtha with a boiling point of lower than 170 ℃, phenol oil with a boiling point of 170–210 ℃, wash oil with a boiling point of 210–230 ℃, naphthalene oil with a boiling point of 230–300 ℃, anthracene oil with a boiling point of 300–360 ℃ and asphalt with a boiling point of more than 360 ℃.

Figure 6(a) shows that compared with N_2 atmosphere, CH_4, H_2 and CH_4 + Ni all make the simulated distillation curve of tar move to the low temperature zone, and the moving range is CH_4 +

Ni > H_2 > CH_4. This shows that the tar is transforming to the direction of lightening under CH_4 and H_2 atmosphere, and the component content of light tar is higher in CH_4 + Ni atmosphere. The yield of tar with boiling point lower than 360 ℃ is as follows: CH_4 + Ni > H_2 > CH_4 > N_2. The yield of oil with boiling point lower than 360 ℃ under CH_4 + Ni is 14.3% higher than that under CH_4. **Figure 6(b)** shows the effects of atmosphere and catalyst on tar fraction. It is found that compared with N_2 atmosphere, the contents of light oil, phenol oil, naphthalene oil, wash oil and anthracene oil under the conditions of CH_4, H_2 and CH_4 + Ni are increased, and the increase amount shows that CH_4 + Ni > H_2 > CH_4, while the asphalt content decreases.

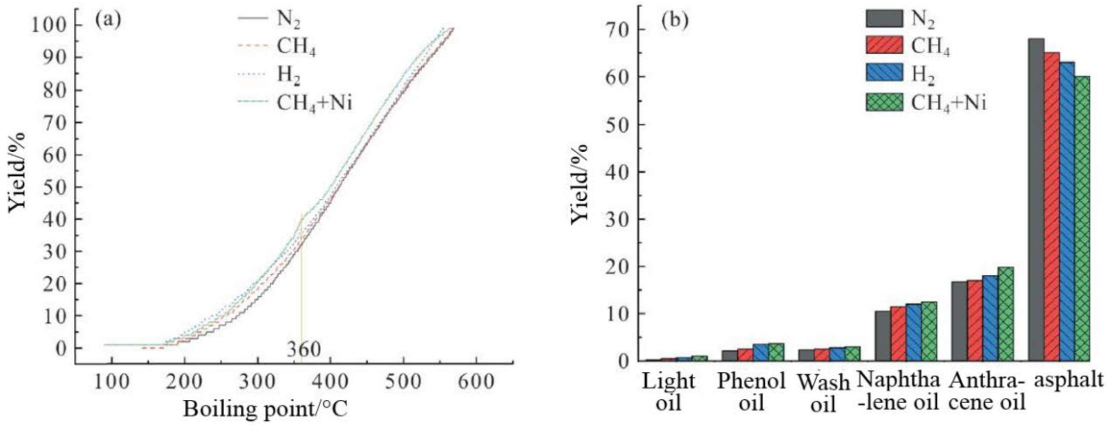

Figure 6. Effects of atmosphere and post-catalyst on tar simulated distillation curve **(a)** and tar fraction **(b)**.

Table 2 shows the GC-MS analysis of pyrolysis tar at 600 ℃. It can be seen from **Table 2** that there are more aromatic hydrocarbons in tar under N_2 atmosphere, with a relative content of 48.14%, followed by aliphatic hydrocarbons and phenols, while the content of oxygen-containing non-phenolic aromatic hydrocarbons is relatively small. Compared with N_2 atmosphere, the relative content of aromatic hydrocarbons in tar in CH_4 and H_2 atmosphere is lower, while the relative content of aliphatic hydrocarbons increases, which indicates that aromatic hydrocarbons are transformed into aliphatic hydrocarbons in reducing atmosphere, because some aromatic hydrocarbons will be converted into aliphatic hydrocarbons by addition reaction under the action of hydrogen free radicals. Compared with CH_4 atmosphere, the addition of post Ni-based catalyst in CH_4 atmosphere will greatly increase the relative contents of aromatic hydrocarbons and aliphatic hydrocarbons, while the phenolic substances will be greatly reduced. This is because CH_4 produces a large number of methyl, methylene and hydrogen free radicals under the action of Ni-based catalyst, which react when contacting with gas-phase tar, so that some phenolic substances are reduced to aromatic hydrocarbons. At the same time, under the action of Ni-based catalyst, aliphatic hydrocarbons also broke, resulting in a further increase in the relative content of aliphatic hydrocarbons. Compared with N_2 atmosphere, the relative content of heteroatom compounds in tar under the conditions of CH_4, H_2 and CH_4 + Ni is reduced, indicating that CH_4 and H_2 atmosphere can remove heteroatoms to a certain extent.

Table 2. GC-MS analysis of pyrolysis tar at 600 ℃

Atmosphere	**Relative content %**					
	Aromatic hydrocarbons	**Phenols**	**Oxygenated non-phenolic aromatic**	**Aliphatic hydrocarbons**	**Alcohols, ketones, ethers, acids**	**Heteroatom compounds**
N_2	48.14	16.39	6.87	19.35	0.81	8.43
CH_4	38.95	29.27	4.22	22.29	0.79	4.48
H_2	45.70	17.68	2.90	25.36	0.54	7.82
CH_4 + Ni	46.50	14.44	3.38	27.37	1.78	6.52

4. Conclusion

(1) Compared with N_2 atmosphere, both CH_4 and H_2 can improve the conversion of coal pyrolysis, and the promotion effect of H_2 is more obvious. H_2 reduces the yield of semi-coke while improves the yield of tar, water and gas. The effect of CH_4 on the four products is basically the same as that of H_2, but CH_4 will decompose at high temperature, resulting in an increase in the yield of semi-coke at high temperature compared with N_2 atmosphere.

(2) H_2 atmosphere can obviously promote the formation of CH_4. Compared with N_2 atmosphere, both CH_4 and H_2 atmosphere are conducive to the formation of C_2–C_3. H_2 atmosphere increases the yield of CO and reduces the yield of CO_2. The yield of H_2 in CH_4 atmosphere is higher.

(3) Compared with CH_4 atmosphere, the addition of post Ni-based catalyst in CH_4 atmosphere increases the tar yield by 10%, the gas yield and the H_2 yield is increased, and the tar is transformed to the direction of lightening. Compared with N_2, CH_4, H_2 and CH_4 + Ni increased the relative contents of light oil, phenol oil, naphthalene oil, wash oil and anthracene oil, and the increase showed that $CH_4 + Ni > H_2 > CH_4$, while the asphalt content decreased. Compared with CH_4, CH_4 + Ni greatly increases the relative content of aromatic hydrocarbons and aliphatic hydrocarbons in tar.

Acknowledgements

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Conflict of interest

The authors declare that they have no conflict of interest.

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