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 N2, CH4 and H2 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 H2 and CH4 atmosphere can improve the conversion of coal pyrolysis and improve the yield of pyrolysis tar. Compared with CH4 atmosphere, the post placed Ni-based catalyst in CH4 atmosphere can increase the tar yield by 10%, increase the gas yield and H2 yield, and transform the pyrolysis tar to the light direction. Through simulated distillation and GC-MS analysis, compared with N2 atmosphere, CH4, H2 atmosphere and CH4 + Ni increased the relative contents of naphtha, phenol oil, naphthalene oil, wash oil and anthracene oil, and the increase showed that CH4 + Ni > H2 > CH4, while the asphalt content decreased. Compared with CH4, the relative contents of aromatic hydrocarbons and aliphatic hydrocarbons increased significantly under CH4 + Ni.

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

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 N2 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 H2 concentration, the yield of tar increases monotonously, and the aromatic hydrocarbons and phenolic compounds in tar also increase[4]. However, the high cost of H2 restricts the development of hydro pyrolysis[5,6]. CH4 with high hydrogen carbon ratio and relatively low cost will replace H2 in coal pyrolysis technology[4]. Coal pyrolysis in fixed bed CH4 atmosphere shows CH4 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 CH4, and the tar yield will be flui-
dized bed CH₄, 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. CH₄ 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/Al₂O₃ 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/Al₂O₃ and 5% Fe/Al₂O₃, 5% Ni/Al₂O₃ obtained light tar with higher content and yield. Li [10] found that adding pre-Mo/HZSM-5 in CH₄ 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 CH₄ + N₂ 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, CH₄, H₂ 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 N₂, CH₄ and H₂ 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.

| 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/Al₂O₃ is prepared by equal volume impregnation [11]. It is impregnated with Ni (NO₃)₂·6H₂O 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.
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 formulas:

\[ Y_{\text{char}} = \frac{W_{\text{char}} - W \times A}{W \times (1 - A - M)} \times 100\% \]  
\[ Y_{\text{tar}} = \frac{W_{\text{tar}}}{W \times (1 - A - M)} \times 100\% \]  
\[ Y_{\text{water}} = \frac{W_{\text{water}} - W \times M}{W \times (1 - A - M)} \times 100\% \]  
\[ Y_{\text{gas}} = \frac{V_{\text{gas}}}{W \times (1 - A - M)} \times 100\% \]  

In the equation: $Y_{\text{char}}, Y_{\text{tar}}, Y_{\text{water}}$ and $Y_{\text{gas}}$ are the yields of semi-coke, tar, water and gas respectively (calculated on dry ash free basis); $W_{\text{char}}, W_{\text{tar}}$ and $W_{\text{water}}$ are the quality of semi-coke, tar and water respectively; $V_{\text{gas}}$ 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 \( \text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_6 \) and \( \text{H}_2 \) 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 \( \text{CH}_2\text{Cl}_2 \) 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 \( \text{CS}_2 \) and then injected. The temperature rise procedure of GC is: the initial temperature is 35 °C and maintained at 35 °C 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, \( \text{H}_2 \) (40 mL/min) and \( \text{N}_2 \) (25 mL/min) are combustion gas and \( \text{N}_2 \) (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 (\( \text{N}_2, 60\% \text{ CH}_4, 60\% \text{ N}_2 + 40\% \text{ H}_2 \)), abbreviated as \( \text{N}_2, \text{CH}_4, \text{H}_2 \) for convenience) and post catalyst \( \text{Ni/Al}_2\text{O}_3 \) 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 decreases gradually with the increase of pyrolysis temperature. Compared with \( \text{N}_2 \) atmosphere, the yield of semi-coke in \( \text{H}_2 \) atmosphere decreases, and the trend is basically the same as that in \( \text{N}_2 \) atmosphere. In the process of coal pyrolysis, the activated hydrogen free radicals provided by the \( \text{H}_2 \) 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 \( \text{N}_2 \), \( \text{CH}_4 \) atmosphere reduces the yield of semi-coke in the low temperature section lower than 600 °C, indicating that \( \text{CH}_4 \) atmosphere promotes the coal pyrolysis reaction at low temperature. However, the degree of \( \text{CH}_4 \) atmosphere promoting coal pyrolysis at low temperature is not as good as that of \( \text{H}_2 \) atmosphere, which indicates that the nature of \( \text{CH}_4 \) 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 \( \text{CH}_4 \) atmosphere increases the yield of semi-coke. Because there are two competitive reactions of \( \text{CH}_4 \) atmosphere on coal pyrolysis: on the one hand, the free radicals generated by \( \text{CH}_4 \) 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 oth-
er hand, decomposition of methane occurs at high temperature \( \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \), 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 \( \text{N}_2 \) and \( \text{H}_2 \) atmosphere, and reaches the maximum at 600 °C. Under \( \text{CH}_4 \) atmosphere, the tar below 700 °C meets the trend of first increasing and then decreasing, while the tar yield is higher than 700 °C at 800 °C. This is related to the previous \( \text{H}_2 \) production from methane cracking at high temperature. \( \text{CH}_4 \) cracking at 800 °C produces a large amount of \( \text{H}_2 \), so the tar yield is further improved compared with 700 °C. Compared with \( \text{N}_2 \) atmosphere, \( \text{CH}_4 \) and \( \text{H}_2 \) atmosphere can promote the increase of tar yield, and the promotion effect of \( \text{H}_2 \) 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 \( \text{H}_2 \) 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 \( \text{N}_2 \) atmosphere, \( \text{H}_2 \) atmosphere and \( \text{CH}_4 \) atmosphere promote the formation of pyrolysis water, and the yield of water in \( \text{H}_2 \) 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 °C to 800 °C, 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$_3$O-, 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$_2$O + 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 °C 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 °C, 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 °C, 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 H₂ in pyrolysis gas\textsuperscript{[17]}. With the increase of pyrolysis temperature, the H₂ yield increases gradually and slowly. Compared with N₂ atmosphere, H₂ yield in CH₄ atmosphere increased significantly with temperature. At 700 °C and above, the high temperature decomposition of CH₄ in the carrier gas becomes the main source of H₂.

3.3 Effect of post catalyst on the yield of pyrolysis products

Figure 4 shows the effect of post catalyst Ni/Al₂O₃ on the yield of pyrolysis products. Figure 4(a) shows that under the action of post catalyst Ni/Al₂O₃, 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 CH₄\textsuperscript{[18]}. Due to the existence of Ni based
catalyst, CH₄ 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 H₂ yield. The results showed that Ni-based catalyst promoted H₂ precipitation at various pyrolysis temperatures, especially at 600 °C and 800 °C. At 700 °C, Ni-based catalyst has no obvious effect on H₂ yield.

**Figure 5.** The effect of post catalyst on H₂ 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 N₂, CH₄, H₂ and CH₄ + Ni at 600 °C were analyzed as representative data. According to ASTM D2887 method, tar is divided into naphtha with a boiling point of lower than 170 °C, phenol oil with a boiling point of 170–210 °C, wash oil with a boiling point of 210–230 °C, naphthalene oil with a boiling point of 230–300 °C, anthracene oil with a boiling point of 300–360 °C and asphalt with a boiling point of more than 360 °C.

**Figure 6(a)** shows that compared with N₂ atmosphere, CH₄, H₂ and CH₄ + Ni all make the simulated distillation curve of tar move to the low temperature zone, and the moving range is CH₄ +
Ni > H₂ > CH₄. This shows that the tar is transforming to the direction of lightening under CH₄ and H₂ atmosphere, and the component content of light tar is higher in CH₄ + Ni atmosphere. The yield of tar with boiling point lower than 360 °C is as follows: CH₄ + Ni > H₂ > CH₄ > N₂. The yield of oil with boiling point lower than 360 °C under CH₄ + Ni is 14.3% higher than that under CH₄. Figure 6(b) shows the effects of atmosphere and catalyst on tar fraction. It is found that compared with N₂ atmosphere, the contents of light oil, phenol oil, naphthalene oil, wash oil and anthracene oil under the conditions of CH₄, H₂ and CH₄ + Ni are increased, and the increase amount shows that CH₄ + Ni > H₂ > CH₄, while the asphalt content decreases.

Table 2 shows the GC-MS analysis of pyrolysis tar at 600 °C. It can be seen from Table 2 that there are more aromatic hydrocarbons in tar under N₂ 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 N₂ atmosphere, the relative content of aromatic hydrocarbons in tar in CH₄ and H₂ 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 reaction under the action of hydrogen free radicals. Compared with CH₄ atmosphere, the addition of post Ni-based catalyst in CH₄ atmosphere will greatly increase the relative contents of aromatic hydrocarbons and aliphatic hydrocarbons, while the phenolic substances will be greatly reduced. This is because CH₄ 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 N₂ atmosphere, the relative content of heteroatom compounds in tar under the conditions of CH₄, H₂ and CH₄ + Ni is reduced, indicating that CH₄ and H₂ atmosphere can remove heteroatoms to a certain extent.

| Atmosphere | Aromatic hydrocarbons | Phenols | Oxygenated non-phenolic aromatic | Aliphatic hydrocarbons | Alcohols, ketones, ethers, acids | Heteroatom compounds |
|------------|-----------------------|---------|---------------------------------|------------------------|---------------------------------|----------------------|
| N₂         | 48.14                 | 16.39   | 6.87                            | 19.35                  | 0.81                            | 8.43                 |
| CH₄        | 38.95                 | 29.27   | 4.22                            | 22.29                  | 0.79                            | 4.48                 |
| H₂         | 45.70                 | 17.68   | 2.90                            | 25.36                  | 0.54                            | 7.82                 |
| CH₄ + Ni   | 46.50                 | 14.44   | 3.38                            | 27.37                  | 1.78                            | 6.52                 |
4. Conclusion

(1) Compared with N2 atmosphere, both CH4 and H2 can improve the conversion of coal pyrolysis, and the promotion effect of H2 is more obvious. H2 reduces the yield of semi-coke while improves the yield of tar, water and gas. The effect of CH4 on the four products is basically the same as that of H2, but CH4 will decompose at high temperature, resulting in an increase in the yield of semi-coke at high temperature compared with N2 atmosphere.

(2) H2 atmosphere can obviously promote the formation of CH4. Compared with N2 atmosphere, both CH4 and H2 atmosphere are conducive to the formation of C2-C3. H2 atmosphere increases the yield of CO and reduces the yield of CO2. The yield of H2 in CH4 atmosphere is higher.

(3) Compared with CH4 atmosphere, the addition of post Ni-based catalyst in CH4 atmosphere increases the tar yield by 10%, the gas yield and the H2 yield is increased, and the tar is transformed to the direction of lightening. Compared with N2, CH4, H2 and CH4 + Ni increased the relative contents of light oil, phenol oil, naphthalene oil, wash oil and anthracene oil, and the increase showed that CH4 + Ni > H2 > CH4, while the asphalt content decreased. Compared with CH4, CH4 + Ni greatly increases the relative content of aromatic hydrocarbons and aliphatic hydrocarbons in tar.

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Conflict of interest

The authors declare that they have no conflict of interest.

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