Research Article

Combustion Characteristics and Combustion Kinetics of Dry Distillation Coal and Pine Tar

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The samples of dry distillation pine tar and coal tar were investigated by TG-DTG-DSC, and the combustion characteristics and combustion kinetics of the samples were studied. The results show that there exist two significant mass loss peak and endothermic peak in the combustion of dry distillation coal tar and pine tar, which, respectively, means the volatile hydrocarbon combustion and heavy hydrocarbon combustion. At the first DTG peak range, the activation energy of dry distillation pine tar and coal tar is about the same at the initial stage (before DTG peak). Activation energy of the dry distillation pine tar increases sharply while that of dry distillation coal tar has little changes on the subsequent stage (after DTG peak). Dry distillated coal tar has better ignition performance, combustible characteristic, combustible stability, and integrated combustion characteristic, but difficult to burnout compared to the dry distillation pine tar.

1. Introduction

The composition of tar is complex, which has an equivalent calorific value of standard coal. Energy content accounts for 5-15% of the total energy of gasification gas [1]. Therefore, it has greatly increased the available energy loss of the gasification technology. On the other hand, tar is extremely easy to adhere to gasification and transportation equipment, which will hinder the normal work of gasification equipment and the system, reduce the gasification efficiency, and increase the available energy loss [2-5]. Serious adhesion even leads to the failure of the gasification system [6-8]. So the processing of the tar in gasification to strengthen the utilization of resources has become the bottleneck of the development of the technology.

There are research reports on thermodynamic and dynamic of biological oil based on a thermogravimetric analysis method locally and internationally. Guo and Yan [9] calculated activation energies based on the thermal weight loss curves of biooil determined by the analytical method of TGA-DTA. Branea et al. [10] studied the process of thermogravimetric reaction of biooil in an air atmosphere, and the whole process was simulated using parallel first-order reaction. Wang et al. [11] compared the pyrolysis characteristics of the component model of biooil, and its three kinds of heavy fraction, activation energy, and frequency factor are gained. Ma et al. [12] analyzed mass loss and endothermic or exothermic peaks by TG-DSC experiment, which provided bases for the catalytic cracking mechanism of biooil model compounds. Most of these studies used a particular component or a mixture of several components of tar as a model compound to study. They can reflect the thermodynamic and dynamic properties of tar in an air and nitrogen atmosphere well and be beneficial to improve biomass gasification operation conditions and reduce the tar production on one aspect, but the experimental results have a degree of being idealized and one-sided [13-15]. Zeng [16] compared the pyrolysis characteristic of biomass, biomass tar, gangue, and sludge and concluded the kinetic parameters of their various stages of the reaction. Dai [17] compared the
combustion characteristic and kinetic of biomass and coal. Liu et al. [18] studied the combustion kinetic characteristics of dry distillation coal tar. There is shortage of the difference between dry distillation pine tar and coal tar.

In the present study, the samples of dry distillation pine tar and coal tar were investigated by TG-DTG-DSC, and combustion characteristics and combustion kinetics were studied, which is both helpful in determining the thermodynamic and kinetic conditions in tar combustion and pyrolysis process and promoting efficiency and lowering the cost of the gasification technique in biomass processing.

2. Experimental Details

2.1. The Experimental Apparatus. Pine tar is brown or black viscous liquid (or semisolid) with particular odor. It is a kind of complicated compound and slightly soluble in water. Its main ingredients are guaiacol, cresol, methyl phenol, phenol, ethyl phenol, turpentine, rosin, etc. Its relative density is 1.03-1.07 kg/L, and its boiling point is 240-400°C.

Coal tar for experiments was low-temperature coal tar and was black viscous liquid with special odor in normal temperature. It contained aromatic hydrocarbons (like benzene, toluene, xylene, naphthalene, and anthracene), aromatic oxygen-containing compounds (e.g., phenol and other phenolic compound), and heterocyclic compounds containing nitrogen and sulfur and many other organic compounds. Its relative density was 1.02-1.23 kg/L, and its boiling point was 450-650°C and it was slightly soluble in water.

2.2. The Experimental Process and Requirements. Thermogravimetric experiments were carried out in a STA499F3 simultaneous thermal analyzer made by Germany NETZSCH Company. In the experiment, the Al2O3 crucible was placed on the thermal balance holder of the thermal analyzer; after leveling, a certain amount of tar was put into the crucible and its surface was smoothed before the thermogravimetric analysis starts.

The instruments were controlled by the computer program, and the variation signals of sample quality changing with time were collected online. The program set the heating rate as 20°C/min from ambient temperature 25°C to 900°C. The pressure of N2 was 0.05 MPa, the N2 flow rate was 40 mL/min, the pressure of O2 was 0.03 MPa, and the O2 flow rate was 10 mL/min.

3. Sample Combustion

Thermogravimetric Characteristics

Figures 1 and 2 are, respectively, the weight loss (TG) curve and thermal weightlessness rate curve of dry distillation of pine and coal tar. Sample flammability could be analyzed by the thermogravimetric rate curve. That is, making a perpendicular line of the peak point on DTG curves can determine the corresponding temperature of the peak point. The corresponding point on the TG curve will be figured out based on that temperature. The points of TG tangent to curve and TG curve initial segment of the parallel lines intersect at one point, and the intersection point corresponds to the temperature of the ignition [19]. The lower the ignition temperature of the specimen is, the more easily the specimen would flame. Conversely, the flammability is more difficult, and the combustion characteristic is the worse. According to the above method of drawing, the pine tar and coal tar ignition temperature was 254°C and 184°C, respectively. Therefore, dry distillation coal tar has better ignition performance.

In Figure 2, the TGA curves of samples showed three peaks. The light hydrocarbon volatilizes and combusts by gasification and pyrolysis, while the residual part would burn directly. The combustion performance of the residual part is different and leads to multiple peak appearance, which also reflects the difficult-to-burnout characteristics of the tar. In comparison, the intermediate section of the peak of carbonization tar is not significant and has smooth transition with the previous peak, which can be used as a combustion peak. The next peak showed rapid combustion of light components after further pyrolysis of residual fractions, while the heavy components are in need of higher temperature to combust. The pyrolysis combustion partition of coal tar residual fractions of dry distillation was significant. The transition of the pyrolysis product after the combustion heat loss rate changes relatively smooth. The weight loss at different temperature sections of the sample in the combustion process is shown in Table 1.

Table 1 shows that before the ignition point, light volatile hydrocarbon content of coal tar is higher than that of pine tar, which is conducive to ignition. At 1# peak, combustion share of dry distillation of pine tar is significantly higher than that of dry distillation of coal tar. There exist great differences in the temperature interval and combustion dynamic factors.

Figure 3 is DSC curves of dry distillation of pine and coal tar. The curves show that there exist two significant endothermic peaks in the combustion of dry distillation coal tar and pine tar, which, respectively, means the volatile hydrocarbon combustion and heavy hydrocarbon combustion. The endothermic curve of pine tar is lower than that of coal tar in the pyrolysis process. Heat absorption of dry distillation pine tar increased significantly when the heavy
hydrocarbon underwent pyrolysis and combustion. Thus, the combustion characteristic of dry distillation pine tar is poorer than that of dry distillation coal tar, which also shows that tar produced in the biomass gasification process is difficult to deal with.

4. Sample Analysis of Combustion Kinetic Characteristics

4.1. Analysis of the Combustion Kinetic Model of Tar. The activation energy is a very important reaction kinetic parameter. It essentially describes the flammability properties of the samples [20]. The oxidation rate is determined by the activation energy [21]. In general, the less the activation energy is, the fewer the energy is required to change the original molecular structure of the reactant, and the stronger the reaction ability, the lower the ignition temperature and the quicker the combustion would be. Conversely, the bigger the activation energy is, the higher the ignition temperature and the slower the combustion would be.

According to the combustion thermogravimetric analysis, the first DTG peak combustion has great influence on the tar combustion dynamic characteristics. So based on the first kinetic differential equation of thermal analysis, there is

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp \left(-\frac{E}{RT}\right).
\]  

In the formula, \( E \) represents the activation energy (J/mol); \( R \) is the equilibrium constant for reactions of ideal gases, and normally its value is 8.314 J/(mol·K); \( T \) represents the thermodynamic temperature (K); \( \alpha \) represents the combustible material share of already combustions (%); \( A \) represents the frequency factor; \( \beta \) represents the heating rate at thermogravimetric experiment (°C/min); \( f(\alpha) \) is the function related to the tar reaction share, supposed \( f(\alpha) = (1 - \alpha)^n \); and \( n \) is the chemical reaction rate.

In general, the value of \( E \) is far bigger than the initial experimental value of \( RT_0 \), so \( \exp \left(-\frac{E}{RT_0}\right) \approx 0 \). After the variable separation and reorganization of formula (1), there is

\[
\ln \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT}. 
\]  

After the constant transformation,

\[
a = -\frac{E}{R}, \quad b = \ln \frac{AR}{\beta E}. 
\]  

That is,

\[
y = ax + b. 
\]  

After the corresponding thermogravimetric experimental data was put into the formula, that is,

\[
y_i = \ln \int_0^{x_i} \frac{d\alpha}{(1 - \alpha)^n T^2}, \quad x_i = \frac{1}{T_i}. 
\]
In the formula, \( i \) is the ordinal of the experimental measurement. Based on the principle of the least square method, the corresponding combustion reaction kinetic parameters can be obtained.

The linear correlation coefficient \( r \) is

\[
 r = \frac{\sum_{i=1}^{m} (y_i \cdot x_i) - \sum_{i=1}^{m} y_i \cdot \sum_{i=1}^{m} x_i}{\sqrt{\left[ m \cdot \sum_{i=1}^{m} y_i^2 - \left( \sum_{i=1}^{m} y_i \right)^2 \right] \left[ m \cdot \sum_{i=1}^{m} x_i^2 - \left( \sum_{i=1}^{m} x_i \right)^2 \right]}}.
\]

4.2. Dry Distilled Coal Tar Combustion Kinetic Characteristics. Figures 4 and 5 represent the coal tar fitting curve to kinetic parameters at peak DTG1#. The peak temperature is 250°C. Figure 4 shows that the combustion reaction rate \( n \) has little influence on the fitting curve in the 184–250°C section. The linear fitting curve through the calculation value \((x, y)\) of measured points of different reaction rates is basically through the reaction rate of 1.

Figure 5 shows that the combustion reaction rate has great influence on the fitting curve in the 250-384°C section. The correlation coefficient curve is basically through the reaction rate of 2. For the reaction order farther from \( n = 2 \) the linear correlation between the fitted scatter points is worse.

The relationship between correlation coefficient \( r \) and reaction rate \( n \) changed significantly in the combustion temperature section of dry distilled coal tar at no. 1 peak where the heat loss rate reduced, and at the point \( n = 2 \), a great relevance appeared. Thus, the combustion reaction rate of dry distilled coal tar at the no. 1 peak should be, respectively, 1 and 2, and the reaction kinetic parameters are shown in Table 2.

Table 2 shows that the activation energy of the initial stage before the DTG peak is about the same as that of the subsequent stage after the DTG peak (2.8% increase).

| \( n \) | \( E \) (kJ/mol) | \( A \) |
|---|---|---|
| 184-250 | 31.917 | 3.312 |
| 250-384 | 32.817 | 5.026 |
4.3. Dry Distilled Pine Tar Combustion Kinetic Characteristics. Figures 7 and 8 represent the pine tar fitting curve of kinetic parameters at peak DTG no. 1. The peak temperature is 331°C. Figure 7 shows that the linear fitting curve through the calculation value \((x_i, y_i)\) of measured points of different reaction rates is basically nearby the reaction rate of 1 at the 254-331°C section but is not as remarkable as that of dry distillated coal tar. And the corresponding fitting point of different reaction rates is more divergent.

Figure 8 shows that the combustion reaction has great influence on the fitting curve in the 331-447°C temperature section. The calculation value \((x_i, y_i)\) distribution of measured points of different reaction rates is more dispersed, and the fitting point of the same reaction rate is not in the same straight line. In the low-temperature section, the scatter line of the same reaction rate is more inclined. Obviously, this is the presence of the overlapped peaks. That is, in the late part of the combustion section, there exists an overlap of the tar pyrolysis combustion and the superposition combustion. The linear fitting curve is in the vicinity of the reaction rates of 2.9 and 3.

The relationship between the reaction rate of dry distillated pine tar at the no. 1 peak DTG in the combustion kinetic model and the correlation coefficient \((r)\) of the fitting linear curve based on the least squares is shown in Figure 9. In the initial stage of combustion, dry distillated pine tar has the similar reaction rate as distilled coal tar. The smaller the value of \(n\) is, the closer the linear correlation coefficient \(r\) will be to 1. Basically, when \(n = 1\), the correlation coefficient curve is relatively horizontal, and the fitting result is more reliable. It is consistent with combustion conditions of the distilled pine tar and the distilled coal tar in the initial stage of combustion, which is caused by light volatile hydrocarbon combustion.

In the combustion temperature section at the no. 1 peak where the heat loss rate reduced, with the increase in the reaction rate \(n\), the curve becomes more horizontal, which means that the correlation coefficient \(r\) of dry distillated pine tar converges with the increase in the reaction rate, but it does not converge to 1. This is due to the existence of two combustion mechanisms in this period. As far as the fitting results of Figure 7 were concerned, the combustion reaction rate \((n = 3)\) is reasonable, and the dry distilled pine tar kinetic parameters are shown in Table 3.

Table 3 shows that the activation energy of the initial stage before the DTG peak is about 24.5% compared to that of the subsequent stage after the DTG peak.

Based on the analysis of Tables 2 and 3, distilled tar combustion activation energy is higher at the DTG no. 1 peak.
peak. The follow-up combustion activation energy should be even bigger at the DTG peak. Therefore, the dynamic combustion is the main part in dry distillated tar combustion with diffusive combustion as a supplement. Dry distillated pine tar has a more complicated reaction mechanism than distillated coal tar, and dry distillated pine tar requires higher reaction activation energy.

5. Sample Analysis of Combustion Characteristics

In order to study combustion characteristics of dry distillation coal tar and dry distillation pine tar, ignition characteristics (gained in the previous analysis, named \(T_i\)), combustible characteristics, combustible stability, burnout characteristics, and integrated combustion characteristics were studied by the TGA.

5.1. Combustible Characteristics and Combustible Stability

Combustible characteristics \(C_b\) [22] and combustible stability \(G\) can be solved by following formulas:

\[
C_b = \frac{(dG/dt)_{\text{max}}}{T_i^2}, \quad G = \frac{(dG/dt)_{\text{max}}}{T_i \times T_{\text{max}}}. (7)
\]

In the formula, \((dG/dt)_{\text{max}}\) is the maximum weight loss rate (%/min), \(T_{\text{max}}\) is the temperature of the maximum weight loss rate (K), and \(T_i\) is the ignition temperature (K).

5.2. Burnout Characteristics

Burnout characteristics \(C'_b\) [23] can be expressed as follows:

\[
C'_b = \frac{f_1 \cdot f_2}{\tau_0}. (8)
\]

In the formula, \(f_1\) is the burn-off rate of the initial state (%) and reflects the relative content of easy volatile light hydrocarbon of the tar, \(f_2\) is the burn-off rate of the latest state (%) and reflects the burnout characteristics of heavy hydrocarbon of the tar, and \(\tau_0\) is the time from the beginning of weight loss to the 98% of the weight loss rate (min).

5.3. Integrated Combustion Characteristics

Integrated combustion characteristics \(S_N\) [22] can comprehensively evaluate the combustion performance of the sample.

\[
S_N = \frac{(dG/dt)_{\text{max}} \cdot (dG/dt)_{\text{mean}}}{T_i^2 \times T_h}. (9)
\]

In the formula, \((dG/dt)_{\text{mean}}\) is the average combustion speed of flammable mass (%/min) and \(T_h\) is the temperature of burnout (K).

Based on the analysis of Table 4, the dry distillated coal tar is easy to be ignited. And its combustible characteristic, combustible stability, and integrated combustion characteristics are better than those of dry distillated pine tar. But burnout characteristics of dry distillated pine tar have better performance. It means that pyrolysis condensation products of dry distillated pine tar are easier to burn out. And the maximum burnout temperature is lower than that of the coal tar.

6. Conclusions

(1) The DTG curves and DSC curves show that there exist two significant peaks, mass loss peak and endothermic peak, in the combustion of dry distillation coal tar and pine tar, which, respectively, means the volatile hydrocarbon combustion and heavy hydrocarbon combustion. The DSC curve of pine tar is lower than that of coal tar in the pyrolysis process, which means that the combustion characteristic of dry distillation pine tar is poorer than that of dry distillation coal tar.

(2) The combustion kinetic characteristics of dry distillated tar depend mainly on the volatility at the first DTG peak range. The activation energy of dry distillation pine tar and coal tar is about the same at the initial stage of combustion (before the DTG peak), but the subsequent combustion kinetic characteristics are different. Coal tar has little changes in the main combustion phase, but the pine tar changes much on the subsequent combustion (after the DTG peak). Its activation energy increases sharply.

(3) The dry distillated coal tar is easy to be ignited. And its combustible characteristic, combustible stability, and integrated combustion characteristics are better than those of dry distillated pine tar. But the burnout characteristics of dry distillated pine tar are better.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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