Study on the Pyrolysis Characteristics and thermal Kinetics of Tea

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Abstract. The pyrolysis characteristics of tea under nitrogen atmosphere were investigated, and the heating rate was 5, 10, 15, 20, 25 °C/min. The Kissinger and FWO methods were used to calculate the pyrolysis activation energy of tea. The results showed that the pyrolysis of tea can be divided into three pyrolysis stages: dehydration stage, rapid pyrolysis stage and carbonization stage. As the heating rate increasing, the peak temperature of the maximum pyrolysis rate shifts to the higher temperature, and the conversion rate increased at the peak of the maximum pyrolysis rate. The average value of pyrolysis activation energy of tea was 193.59 kJ/mol.

1. Introduction

Tea, coffee, and cocoa are called the world's three major beverages. With the rapid development of economy, the tea industry has continued to grow steadily in China. In the normal production process of tea, a certain amount of low-grade tea and by-products are often produced. Due to production technology and sales problems, many low-end teas become unsaleable, which will seriously restrict the growth and development of the tea industry. In recent years, more researches have focused on the utilization of the low-value tea, such as the extraction of tea functional ingredients, tea health care products, etc [1].

Biomass pyrolysis refers to the thermal decomposition of substances by heating under the conditions of anoxic or anaerobic conditions. The biomass pyrolysis of low-value tea can be converted into clean energy to alleviate the energy crisis and environmental problems [2], meanwhile this method will increase the added value of the tea.

In this study, thermogravimetric analysis was used to portray pyrolysis behavior of the tea, and the effect of the heating rate on the thermal degradation of tea was also studied. A kinetic study was conducted to provide corresponding theoretical basis for the pyrolysis characteristics of tea.

2. Materials and methods

2.1. Experimental materials

Tea were used as biomass samples. Tea was purchased from Shaanxi Xixiang Baiyan Tea Co, Ltd. Before testing, the tea was pulverized to less than 48 um and dried at 103 °C for 2 h.

2.2. Test method

The pyrolysis of the samples was measured at heating rates (β) of 5, 10, 15, 20, and 25 °C, and heating ranges of 30 to 700 °C. All experiments were performed in a N2 atmosphere with a N2 flow of 30 mL/min.
From the mass loss curve (TG) and the mass loss rate curve (DTG), the peak temperature of pyrolysis, the weight loss rate at different temperatures, the corresponding weight loss temperature, and the carbon residue at 700 °C were obtained.

2.3. Kinetics analysis
Kissinger and Flynn-Wall-Ozawa (FWO) methods were used for interpreting resin degradation kinetics, as shown in Eq. 1 and 2, respectively.

Kissinger equation (Eq. 1)

\[- \ln \left( \frac{\beta}{T_p^2} \right) = \frac{E}{RT_p} - \ln \left( \frac{AR}{E} \right)\]

Where \(\beta\) is the heating rate (K/min); \(T_p\) is the peak temperature; \(E\) is the activation energy (kJ/mol).

On the basis of Eq. 1, there is a straight line between \(\ln(\beta/T_p^2)\) and \(1/T_p\); therefore, the activation energy and pre-exponential factor can be calculated from the slope and the intercept, respectively.

FWO equation Eq. 2,

\[\ln \beta = C - 1.0516 \left( \frac{E}{RT_p} \right)\]

There is a linear relation between \(\ln\beta\) and \(1/T_p\), so the activation energy can be calculated from the slope of the linear equation.

3. Results and discussion

3.1. Tea pyrolysis characteristics

The changes of TG and DTG curves of tea under different heating rates are shown in Figure 1. Based on the DTG curve, the mass loss range could be divided into three steps. The obvious mass loss in the first stage occurred before 200 °C. According to the DTG curve, it can be seen that the mass loss rate was the largest at 75-95 °C. The mass loss at this stage was mainly due to the removal of water from the tea. When the temperature rose to 200 °C, the quality of the sample dropped suddenly, which may be the decomposition and volatilization of a small amount of small molecular aroma components (alcohols and ethers) in tea [3]. Mass loss mainly occurred in the second stage, with a mass loss of 60.98%. According to the DTG curve, the weight loss rate of the sample reached the maximum at 315-345 °C. The DTG curve was formed by superposing the pyrolysis peaks of the three components of cellulose, hemicellulose and lignin. It is known that the complete decomposition temperatures of hemicellulose, cellulose and lignin are 210-325 °C, 310-400 °C and 160-900 °C respectively [4-8]. Therefore, the DTG curve appears at 250 °C and 400 °C. The peak may be due to the decomposition of hemicellulose and cellulose. Above 500 °C, the loss of pyrolysis mass of the sample was small, and it can be considered...
as the region of lignin decomposition, because it is known that the decomposition of lignin occurs slowly over a wide temperature range [9].

3.2. Effect of heating rate on the pyrolysis characteristics of tea

| Heating rate (°C/min) | Peak temperature (°C) | Maximum peak conversion rate (mg/min⁻¹) | Char residual at 700 °C (%) |
|-----------------------|-----------------------|------------------------------------------|-----------------------------|
| I                     | II                    | III                                      |                             |
| 5                     | 75.03                 | 242.03                                  | 319.72                      | 1.85                        | 34.44                      |
| 10                    | 68.74                 | 245.74                                  | 328.24                      | 3.65                        | 33.00                      |
| 15                    | 85.04                 | 250.04                                  | 334.23                      | 5.32                        | 34.26                      |
| 20                    | 92.90                 | 266.90                                  | 341.39                      | 6.87                        | 32.88                      |
| 25                    | 93.88                 | 272.88                                  | 342.17                      | 8.24                        | 33.74                      |

As can be seen in Figure 1 and Table 1 that when the heating rate continues to increase, the TG curve coincides with a higher degree and the shape was basically the same, but the heating rate had different degrees of influence on the weight loss process of tea pyrolysis. When the heating rate was increased from 5 °C/min to 25 °C/min, the water analysis temperature and peak temperature both moved slightly to the high temperature side as the heating rate increases, and the peak corresponding temperature shifted to the higher temperature, but the shift amount smaller. This showed that increasing the heating rate can increase the maximum weight loss rate of tea pyrolysis. The reason for this phenomenon may be that there was a heat transfer temperature difference between the tea sample and the measurement point, which caused a thermal hysteresis during the pyrolysis of tea. However, the carbon residue at 700 °C was hardly affected by the thermal hysteresis phenomenon.

3.3. Tea pyrolysis kinetics analysis

According to the linear relationship between \(-\ln(\beta/T_p^2)\) and \(1/T_p\), \(\ln(\beta)\) and \(1/T_p\), perform relevant data fitting, The results were shown in Figure 2.

![Figure 2. Kissinger and FWO plots of tea (a: Kissinger, b: FWO)](image)

| Category | Method  | Fitted equation | E/KJ·mol⁻¹ | A/min⁻¹ | \(R^2\) |
|----------|---------|----------------|------------|---------|--------|
| Tea      | Kissinger | \(y = -23.32x + 28.08\) | 193.92     | 3.66×10¹³ | 0.98   |
|          | FWO     | \(y = -24.44x + 42.89\) | 193.25     | -       | 0.98   |
The Kissinger and FWO methods were used to calculate the pyrolysis kinetics of tea. The results were shown in Figure 2 and Table 2. The higher apparent activation energy values means it would need higher energy to break the chemical bonds, resulting in slower reactions [10]. The larger the apparent activation energy value, the more energy was required to overcome the bond energy barrier. As shown in Table 2, the apparent activation energy value of thermal degradation of tea was relatively large. This indicated that tea has strong thermal stability.

4. Conclusion

The pyrolysis of tea can be divided into three pyrolysis stages: dehydration stage, rapid pyrolysis stage and carbonization stage. As the heating rate increases, the conversion rate increases at the peak of the maximum pyrolysis rate, and the peak temperature of the maximum pyrolysis rate shifts toward the high temperature section.

The Kissinger equation and FWO equation were used to calculate the pyrolysis activation energy values of tea at 193.92 kJ/mol and 193.25 kJ/mol, respectively.

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