Study on the pyrolysis characteristics of walnut processing by-products

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Abstract. Thermogravimetric analysis (TG) was used to study the thermal degradation behaviour of walnut shell and walnut meal during thermal treatment, and the Kissinger and Flynn-Wall-Ozawa equation were used to calculate the activation energy. The heating rate was 5, 10, 15, 20, 25 °C/min with nitrogen atmosphere. The results showed that the thermal degradation process of walnut shell and walnut meal can be divided into three stages: dehydration stage, rapid pyrolysis and carbonization stage. The greater the heating rate was, the faster the thermal degradation became. At the same heating rate, the weight loss rate, the peak conversion rate and the carbon residue in the rapid pyrolysis stage of walnut shell were all greater than those of walnut meal. The activation energy of thermal degradation of walnut shell was 194.54 kJ/mol and 194.50 kJ/mol. The activation energy of thermal degradation of walnut meal was 167.37 kJ/mol and 169.78 kJ/mol. Walnut shell had higher thermal degradation activation energy and thermal stability.

1. Introduction
Walnuts, together with almonds, cashews, and hazelnuts, are the world-famous nuts. The walnut consumption is increasing and the comprehensive utilization of walnut processing by-products has become an unavoidable problem in the walnut processing industry. The traditional methods are mainly stacking, discarding and incineration [1], which not only causes energy waste but also causes severe environmental pollution. Therefore, the comprehensive utilization of walnut processing by-products has become a hot topic.

The walnut processing residues are mainly walnut shell (WS) and walnut dregs (WD). In recent years, there have been many studies on WS and WD, for example: extraction of active substances in WS [2, 3], preparation of activated carbon with WS as raw material [4, 5], and combustion and pyrolysis studies with WS as raw material [6, 7], there are phenolic resins and foams prepared by liquefaction with WS as raw materials [8, 9]. The main components of WS are cellulose, hemicellulose and lignin [8, 9], and the main components of WD are proteins [10, 11], all of which have huge energy development potential. Studying the pyrolysis characteristics of WS and WD is of great significance to the comprehensive utilization of walnut processing by-products. In recent years, researches on the preparation of solid, liquid, and gas three-phase products by pyrolysis using biomass as a raw material have been increasing. Although some researchers have conducted some researches on the pyrolysis characteristics of WS [6, 7], there have been no reports on the pyrolysis characteristics of WD. Therefore, in this study,
thermogravimetric analysis (TG) technology was used to study the pyrolysis characteristics of WS and WD, and Kissinger equation and Flynn-Wall-Ozawa equation were used to study the pyrolysis kinetics and analyze the differences.

2. Materials and methods

2.1. Test materials
Walnut shells (WS) and walnut dregs (WD) were used as biomass samples. Walnut shells were collected in Shanyang County, Shanxi Province, and walnut dregs were purchased from Xi'an Bodaweier Biological Co., Ltd. Before testing, the walnut shell and walnut dregs were pulverized to less than 48 um and dried at 103 °C for 2 h.

2.2. Test method
The thermal degradation 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 nitrogen atmosphere with a flow of 30 mL/min.

2.3. Thermal degradation activation energy
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 β is the heating rate (K/min); Tp is the peak temperature; E is the activation energy (kJ/mol). On the basis of Eq. 1, there is a straight line between ln(β/Tp^2) and 1/Tp; 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 lnβ and 1/Tp, so the activation energy can be calculated from the slope of the linear equation.

3. Pyrolysis characteristics analysis

3.1. Analysis of pyrolysis characteristics of WS

Figure 1. TG and DTG curves of WS
The TG and DTG curves of WS under different heating rates are shown in Figure 1. Based on the DTG curve, the range of WS quality loss can be divided into three regions. The first region starts at 40 °C and ends at 175-190 °C. A slight mass loss (5.56%-6.27%) occurred in this area, which was caused by the removal of water from the WS. The second region with an average mass loss of 52.78%, which started at around 190 °C and ends at around 360-400 °C. The small shoulder of the DTG curve near 220-250 °C showed a slight reaction. Then the main reaction occurred and a strong peak occurred near 315-340 °C. WS is mainly composed of hemicellulose, cellulose and lignin. It is known that hemicellulose, cellulose and lignin complete decomposition in the temperature ranges of 210-325 °C, 310-400 °C and 160-900 °C, respectively [12-15]. Therefore, the huge mass loss that occurs in the active pyrolysis zone can be mainly attributed to hemicellulose and cellulose decomposition. The third zone starts at 400 °C and continues to 700 °C. This zone is referred the passive pyrolysis zone because the mass loss is small and the average mass loss is determined to be 27.17%. This region can be considered as a region where lignin is decomposed, as it is known that decomposition of lignin occurs slowly over a wide temperature range [16]. At the end of the entire thermal degradation process, the average residual mass was determined to be 31.13%.

3.2. Analysis of pyrolysis characteristics of WD

Fig. 2 shows the TG and DTG curves of WD at different heating rates as a function of temperature. The first peak is less than 100 °C, which mainly due to the evaporation of water. The second peak is generated at about 210-225 °C, and the mass loss is about 10.99%. The third peak is generated at about 330-350 °C, and the mass loss is about 53.80%. The fourth peak is the maximum peak, which occurred between 380-420 °C, and the mass loss is 67.11%. It is well known that the three-dimensional structure of a protein is governed by its primary structure, the amino acid sequence [17]. The two main covalent bonds present in proteins are peptide bonds and disulfide bonds. The second peak is due to the elimination of water and the dissociation of the quaternary structure of the protein. The third peak is mainly due to the break of covalent bonds between peptide bonds of amino acid residues. The maximum peak may be caused by the cleavage of the S-S, O-N and O-O bonds of the protein molecule. After 500-700 °C, WD is completely decomposed and forming various gases, such as CO, CO2, NH3, H2S and other gases. Above 710 °C, only char remained [18].
3.3. Effect of heating rate on pyrolysis characteristics

Table 1. Thermal parameters of WS and WD obtained from TG analysis

| Heating rate (°C/min) | Peak temperature (°C) | Maximum peak conversion rate (mg/min⁻¹) | Char residual at 700°C (%) |
|-----------------------|-----------------------|----------------------------------------|---------------------------|
|                       | I                     | II                                     | III                       | IV                        |
| WS                    |                       |                                        |                           |                           |
| 5                     | 59.11                 | 202.11                                 | 316.94                    | 3.16                      | 30.03                     |
| 10                    | 75.99                 | 218.99                                 | 327.89                    | 6.03                      | 32.59                     |
| 15                    | 83.97                 | 225.97                                 | 333.27                    | 8.83                      | 32.68                     |
| 20                    | 92.98                 | 230.98                                 | 337.98                    | 11.70                     | 32.22                     |
| 25                    | 83.82                 | 238.82                                 | 340.36                    | 14.44                     | 29.88                     |
| WD                    |                       |                                        |                           |                           |
| 5                     | 68.11                 | 213.11                                 | 327.11                    | 382.56                    | 2.07                      | 23.38                     |
| 10                    | 74.07                 | 226.07                                 | 339.07                    | 399.26                    | 4.28                      | 24.76                     |
| 15                    | 69.98                 | 227.98                                 | 338.98                    | 401.38                    | 6.30                      | 22.68                     |
| 20                    | 87.97                 | 231.97                                 | 341.97                    | 412.06                    | 8.76                      | 23.12                     |
| 25                    | 85.62                 | 235.62                                 | 347.62                    | 416.41                    | 10.98                     | 22.21                     |

It can be seen from Fig. 1, and Fig. 2, and Tab. 1 that when the heating rate continues to increase, the TG curve coincides with a higher degree and the shapes are basically the same. When the heating rate increased from 5 °C/min to 25 °C/min, the water analysis temperature and peak temperature both moved slightly to the higher temperature. It can be known from the DTG curve that the maximum peak-to-peak value of the DTG curve becomes “sharp” obviously when the heating rate increased, which indicated that the increase of the heating rate could increase the maximum weight loss rate. The temperature corresponding to the peak value shifts to the higher temperature, but the shift amount is not large. This may be due to the heat transfer temperature difference between the WS and WD samples and the measurement points, which results in thermal hysteresis during the pyrolysis of WS and WD. However, the char residue at 700 °C is hardly affected by the thermal hysteresis phenomenon.

3.4. Pyrolysis kinetics analysis

According to the linear relationship between -ln(β/Tp²) and 1/Tp, ln(β) and 1/Tp, perform relevant data fitting. The results are shown in Figs. 3.

![Figure 3. Kissinger and FWO plots of WS and WD (a: Kissinger; b: FWO)](image_url)

The Kissinger and FWO equations were used to calculate the pyrolysis kinetics of WS and WD. The results are shown in Table 2.
Table 2. Using Kissinger method to obtain the relevant data of WS and WD

| Resin | Method | Fitted equation | $E$/KJ·mol$^{-1}$ | A/min$^{-1}$ | $R^2$ |
|-------|--------|-----------------|-------------------|-------------|-------|
| WS    | Kissinger | $y=-23.40x+28.48$ | 194.54 | 5.46×10$^{13}$ | 0.99 |
|       | FWO    | $y=-24.60x+43.28$ | 194.50 | - | 0.99 |
| WD    | Kissinger | $y=-20.13x+19.45$ | 167.37 | 5.08×10$^{9}$ | 0.97 |
|       | FWO    | $y=-21.48x+34.37$ | 169.78 | 0.97 |

Reactions with higher apparent activation energy (E) require higher energy to break chemical bonds, resulting in slower reactions [19]. The larger the E value, the more energy is required to overcome the potential energy barrier. As shown in Table 2, the apparent E value of WS pyrolysis is greater than WD. This indicates that WS has higher thermal stability and WD is more easily Pyrolysis.

4. Conclusion

The pyrolysis conversion rate of WD is larger than that of WS, which is mainly due to the high volatile content of WD.

The Kissinger equation and FWO equation were used to obtain the pyrolysis activation energy of WS and WD. The pyrolysis activation energy of WS is greater than WD, which indicates that WS has better thermal stability.

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