

# Pyrolysis Characteristics and Kinetics of *Prunus avium* L. Leaves using a Thermogravimetric Analyser

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## Article

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# Abstract

To investigate the differences in the pyrolysis characteristics of leaves of sweet cherry tree (*Prunus avium* L.) under rain-shelter cultivation (RS) or under open-field cultivation (CK), thermogravimetric (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) curves were compared at three heating rates of 10, 20 and 30°C·min<sup>-1</sup>. There were two obvious mass loss peaks at 280°C and 330°C, which were manifested by the slow pyrolysis of hemicellulose in the low temperature region and the rapid pyrolysis of cellulose in the high temperature region, respectively. The curve in the pyrolysis range after 440°C was stable, and the mass change corresponded to the pyrolysis of a small amount of macromolecular organic extracts and inorganic salts. When the temperature reached 600°C, approximately 69% and 73% of the CK and RS leaves were thermally destroyed, respectively. The Coats-Redfern method was used for kinetic calculations to obtain an activation energy of 29.75 ~ 36.14 kJ·mol<sup>-1</sup> in the first-order pyrolysis kinetics stage. The second-order pyrolysis kinetics stage can fit the pyrolysis process well. The pyrolysis characteristics and kinetic parameters of the leaves were related to the heating rate and the hemicellulose content, cellulose content and lignin ratio in each sample.

## Introduction

Current societal development is facing the constraints of a lack of fossil fuels and increased environmental pollution. The development and use of renewable energy has become an important choice for solving energy and environmental problems<sup>1</sup>. Biomass energy, as an efficient and renewable natural resource, is an alternative energy source with great development potential<sup>2</sup>. Pyrolysis is one of the most efficient and potential methods for the thermochemical conversion of biomass energy, and it is also an effective way to comprehensively utilize biomass. Exploring thermochemical conversion of the leaves of a deciduous tree is important for optimising the waste fallen leaves. The pyrolysis of raw materials such as biomass in a nitrogen atmosphere can convert the biomass into solid, liquid and gaseous fuels and other chemical fuels or products from renewable carbon sources<sup>3,4</sup>. The study of the pyrolysis kinetics of biomass fuel can reveal the reaction mechanism of the thermochemical utilization process in depth, predict the reaction rate and the difficulty of the reaction, and provide theoretical support for the rational use of biomass energy. Many scholars have studied the industrial applications of thermal conversion of plant leaves. Liang et al. investigated the pyrolysis characteristics of moso bamboo (*Phyllostachys pubescens*), including the outer layer, middle layer, inner layer and leaves, through TG-FTIR and Py-GC/MS. Their results showed that 70% of the mass loss occurred at the rapid pyrolysis stage at temperatures of 200-400 °C<sup>5</sup>. It can be found from the above research that most scholars have typically studied the biomass pyrolysis properties of materials by differential thermal analysis (DTA)<sup>6</sup>. Some researchers have performed research on pyrolysis process parameters<sup>7,8</sup>. Li et al. revealed the decay resistance and physico-chemical behaviour during the heating process of *C. camphora* methanol extracts were discussed by analysing the pyrolysis characteristics and kinetic analysis of sapwood brown rot of *P. Massoniana* treated with *C. camphora* methanol extracts<sup>9</sup>. These studies have often focused on the pyrolysis change characteristics of various biomass materials, but there is no research comparing the pyrolysis performance of plants under different cultivation patterns.

As natural organic matter, sweet cherry (*Prunus avium* L.) leaves are composed of hemicellulose, cellulose, and lignin, as well as volatile oils, crude fats, crude proteins, and minerals (such as inorganic salts)<sup>10,11</sup>. In this study, TGA was used to accurately measure the relationship between leaf mass and temperature under programme-controlled temperature conditions, including the leaf pyrolysis process, determination of moisture content, volatile matter and ash content, dehydration and moisture absorption, and reaction kinetics<sup>12,13</sup>. It's important to explore the differences in the composition of leaves of sweet cherry tree under open-field cultivation (CK) or under rain-shelter cultivation (RS). The pyrolysis of sweet cherry leaves is a process involving complex thermophysical and chemical changes. The analysis and evaluation of the thermal stability and thermodynamic equations of CK and RS leaves are of great significance for exploring the application value of comprehensive resources of sweet cherry and the establishment of industrial development systems.

## Materials And Methods

**Plant material and experimental.** The leaves of sweet cherry variety 'Summit' were collected from the Baiyi fruit tree experimental base of Guiyang Wudang, Guizhou Institute of Fruit Tree Science (27°03'3.89"N and 106°25'47.23"E), and the collection time was July 2019. The rain-shelter facilities are 4 span rain-shelters built in April 2014. The use of plant material, comply with relevant forestry sector, national, and international guidelines and legislation. A voucher specimen (No. 1296) has been deposited in the herbarium of our laboratory. Three trees with normal growth and relatively consistent growth potential were selected randomly from rain-shelter cultivation and open field cultivation, separately, and 20 leaves from four directions were harvested from each tree. After being washed with distilled water, the fresh leaves were oven dried at 105°C for 30 minutes and then dried at 80°C to constant weight. The dried leaves were ground with a mini-pulveriser, and 40 ~ 60 mesh powder was screened as the raw material for the test.

**Thermogravimetric Analysis.** The experiments were carried out in a TG-DSC thermal analyser (NETZSCH STA449F5, Germany) and were purged with N<sub>2</sub> at heating rates of 10, 20, and 30°C·min<sup>-1</sup>. The samples were heated from 30°C to 600°C in an alumina crucible with a diameter of 6.8 mm and a volume of 0.06 mL. During the heating and pyrolysis of the sample, the mass loss was monitored continuously. The onset and inflection temperatures of the pyrolysis were recorded by the analyser for each sample. Data were collected with NETZSCH software and then evaluated using Origin software.

## Results And Discussion

**The Pyrolysis Characteristics.** The pyrolysis characteristics of sweet cherry leaves are shown in Fig. 1 ~ 3. It can be concluded that the RS samples have pyrolysis processes similar to those of the CK leaves. Combining the results of previous studies on wood pyrolysis, the pyrolysis process of sweet cherry leaves under N<sub>2</sub> gas protection at full temperature can be divided into four stages (Fig. 1 (A) a, b, c, d)<sup>14,15</sup>. The first stage is the drying stage (temperature < 140°C), and the thermal gravity analysis (TG) curve shows a gentle curve. At this stage, water precipitation accounts for approximately 5% of the total mass, which is mainly caused by the heat evaporation of free water in the leaves, the physical adsorption of water and crystal water in the molecules, accompanied by the softening and melting of waxy components in the leaves. The second stage is the preheating stage (the temperature range is approximately 140 ~ 220°C), and the TG curve does not decrease much. The mass loss rate at this stage is approximately 5%. The main reason is that the unstable hemicelluloses in the leaves begin to pyrolyze, generating a small amount of CO, CO<sub>2</sub>, H<sub>2</sub> and other gases, and a small amount of depolymerization, internal recombination and 'glass transition' occur<sup>16,17</sup>. The third stage is the pyrolysis stage (the temperature range is approximately 220 ~ 440°C). During this interval, cellulose, hemicellulose and lignin in the sweet cherry leaves are pyrolyzed, and the pyrolysis reaction is intense. The mass loss rate drops sharply at this stage by approximately 50 ~ 55%. The rapid degradation of cellulose and hemicellulose generates a large amount of volatiles and small molecule gas products such as CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. The fourth stage is the carbonization stage (temperature > 440°C), and the TG curve is relatively stable compared with the third stage. The mass loss rate at this stage is relatively small, approximately 7%<sup>18,19</sup>.

TG curves reflect the relationship between the sample mass, temperature and heating rate<sup>20,21</sup>. As seen from the mass loss at 600°C in Fig. 1, the mass loss of the RS leaves under the three heating rates was greater than that of the CK leaves. This outcome indicates that the cellulose, hemicellulose, lignin and other easily pyrolytic organic components in the RS leaves are higher than in the CK leaves. Different heating rates had little effect on the TG of sweet cherry leaves under the same cultivation pattern.

The pyrolysis process of sweet cherry leaves is the result of the combined pyrolysis of hemicellulose, cellulose, lignin and other substances (organic extracts such as macromolecular crude proteins and inorganic salts)<sup>22,23</sup>. In Fig. 2, derivative thermogravimetry (DTG) shows that the DTG curve peak clearly presents three gradients, with the peaks from large to small in the order 30°C·min<sup>-1</sup> > 20°C·min<sup>-1</sup> > 10°C·min<sup>-1</sup>. Under the same heating rate, the DTG of the RS leaves was slightly higher than that of the CK leaves. The greater the heating rate is, the greater the rate of change of its mass with temperature and time. The two samples have a peak in the drying stage near 70°C, which indicates a process of endothermic evaporation of moisture in the samples. When the temperature rose to 140°C, the pyrolysis reaction gradually started, and the DSC curve

decreased. Weak DTG curve fluctuations can be seen at 140 ~ 180°C, which may be due to the precipitation of some volatile oils at lower temperatures. At stage C (220 ~ 440°C), the slope of the sample mass loss curve and the corresponding DTG-T (DTG and temperature) values gradually increase, mainly due to the conversion of cellulose, hemicellulose and lignin, the main components of leaves, into small molecular volatile substances<sup>24</sup>. The DTG obviously undergoes a severe pyrolysis reaction at approximately 280°C and 330°C. Two distinct downward peaks appear at these two positions, and the peak sizes are different. This outcome is mainly due to the pyrolysis of sweet cherry leaves in two stages: the former peak indicates that the pyrolysis of hemicellulose has basically ended and the pyrolysis reaction of lignin has not yet reached the maximum<sup>25</sup>. The latter peak indicates that the pyrolysis reaction of cellulose has reached the maximum. Because of the relative content difference of hemicellulose and cellulose components in sweet cherry leaves, two separate wave peaks appear in the curve<sup>26</sup>. If the hemicellulose content is significantly lower than the cellulose content, the two dispersed wave peaks will form a wide wave peak<sup>27</sup>. The two peaks formed here illustrate the small difference in cellulose and hemicellulose contents in the leaves. After 440°C, as the temperature continues to increase, the mass loss rate decreases rapidly, and the TG and T in the TG-T (TG and temperature) curve have an approximately linear relationship. At this stage, the pyrolysis reaction of the lignin continues, and the DSC curve continues to fall. This outcome shows that there is a certain amount of crude fat and crude protein in the sweet cherry leaves that can only be thermally degraded at high temperatures<sup>28,29</sup>.

Figure 3 (A) shows that each sample mainly absorbed heat before 140°C. After 140°C, the DSC curve gradually becomes negative, and thermal decomposition of the pyrolysis stage of holocellulose (cellulose and hemicellulose) and the pyrolysis stage of lignin begins. The DSC curve trend is relatively flat at 140 ~ 220°C. Hemicellulose begins to pyrolyze, but the activation energy is not high. The DSC curve decreased rapidly at 220 ~ 440°C, mainly due to the rapid pyrolysis of hemicellulose and cellulose and lignin. Figure 3 (B) shows that under the same temperature rising condition, the heat absorbed by the CK leaves is higher than that absorbed by the RS leaves. This outcome shows that the key factors affecting the thermal stability of sweet cherry leaves under the two cultivation patterns are different in hemicellulose, cellulose and lignin content.

**Modelling of Pyrolysis Kinetics.** The mass of the sample (TG) and the changes in heat flux (DSC) were measured. For the common solid phase reaction, the sweet cherry leaf mass loss pyrolysis reaction can be simplified to the following reaction process:  $A \text{ (solid)} \rightarrow B \text{ (solid)} + C \text{ (gas)}$ .

The reaction mechanism function is calculated using the Coast-Redfern equation and the thermal analysis kinetic triplet comparative law:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (n=1) \quad (1)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (n \neq 1) \quad (2)$$

Let  $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$  map  $\frac{1}{T}$  when  $n=1$ , let  $\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]$  map  $\frac{1}{T}$  when  $n \neq 1$ , and we

can generate two lines. The slope is  $-\frac{E}{R}$ , and the ordinate is  $\ln\frac{AR}{\beta E}$ . The activation energy

(E) and pre-exponential factor (A) were calculated using the slope and ordinate.

$\alpha$ : the extent of reaction,  $\alpha = \frac{W_0 - W_t}{W_0 - W_\infty}$ , Heating rate  $\beta = \frac{dT}{dt}$  is a constant, t: reaction

time (min),  $W_0$ : quality before mass loss (mg),  $W_\infty$ : residue quality (mg),  $W_t$ : quality at the beginning of t (mg), Z: pre-exponential factors ( $\text{min}^{-1}$ ), E: activation energies ( $\text{kJ}\cdot\text{mol}^{-1}$ ), R: universal gas constant ( $8.314 \times 10^{-3} \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), T: reaction temperature (K),  $T = 273.15 + ^\circ\text{C}$ .

The theoretical analysis of biomass pyrolysis characteristics is mainly based on the analysis of kinetic processes based on a single-component reaction model or a multicomponent parallel reaction model. Through the calculation of the experimental data, it is found that there are great differences in the pyrolysis kinetics of sweet cherry leaves at different temperature ranges. The pyrolysis behaviour of the samples in the low temperature range ( $220 \sim 440^\circ\text{C}$ ) is consistent with the first-order pyrolysis kinetic rule, and the pyrolysis behaviour in the high temperature region ( $440 \sim 600^\circ\text{C}$ ) meets the second-order reaction kinetic rule (Fig. 4)<sup>30</sup>. The simulation results not only enrich the quantitative understanding of the kinetics of the pyrolysis reaction of sweet cherry leaves but also confirm the reliability of the kinetic analysis technology.

**Thermodynamics Parameters.** The pyrolysis kinetics parameters of holocellulose during pyrolysis and lignin thermal decomposition of sweet cherry leaf samples under different cultivation patterns were calculated under different temperature conditions. According to the experimental data, the fitting equation was calculated in two stages by the Coats-Redfern method, and the pre-exponential factor and activation energy of the two main pyrolysis stages were calculated. The linear correlation coefficients ( $R^2$ ) are all above 0.98, and the linear fitting effect is good. In the first-order pyrolysis reaction stage, the activation energy is  $29.75 \sim 36.14 \text{ kJ}\cdot\text{mol}^{-1}$ , with little difference. This interval mainly involves the pyrolysis of hemicellulose and cellulose. Its activation energy is small compared to the hemicellulose thermogravimetric test results ( $48.5 \sim 88.4 \text{ kJ}\cdot\text{mol}^{-1}$ ) obtained by Orfão<sup>31</sup>. This outcome may be due to the lower content of volatile oils that are easily pyrolyzed in sawdust and bark samples. The activation energy in the second-order pyrolysis reaction stage range is  $32.85 \sim 92.49 \text{ kJ}\cdot\text{mol}^{-1}$  and mainly involves the pyrolysis of lignin, a small amount of organic extracts (such as crude protein, etc.), minerals (inorganic salts, etc.) and other chemically stable substances<sup>32,33</sup>; the specific results are shown in Table 1. Sweet cherry leaves under different cultivation patterns were heated at 3 heating rates, and the activation energy E in the second-order pyrolysis reaction stage is larger than that in the first-order pyrolysis reaction stage. This outcome indicates that the second-order pyrolysis reaction stage mainly involved the pyrolysis of lignin with better thermal stability, while the first stage mainly involved the pyrolysis of hemicellulose and cellulose with relatively unstable structures<sup>34</sup>. Therefore, the activation energy in the first-order pyrolysis reaction stage is smaller than that in the second-order pyrolysis reaction stage. In general, the pyrolysis sequence and trend of the main components of sweet cherry leaves are similar to those of wood. Compared with the RS leaves, the activation energy

of the CK leaves is slightly higher, indicating that the CK leaves had more stable chemical properties, showed good thermal stability and were not easy to pyrolyze.

Table 1  
Thermodynamic parameters of different reaction stages with the Coats-Redfern method

| Samples                                                                                                                                                 | $\beta$<br>Heating<br>rating/( $^{\circ}\text{C}\cdot\text{min}^{-1}$ ) | Reaction<br>stage | T<br>Temperature<br>range/ $^{\circ}\text{C}$ | E<br>Activation<br>energy/( $\text{KJ}\cdot\text{mol}^{-1}$ ) | A<br>Pre-<br>exponential<br>factor/ $\text{min}^{-1}$ | Fitting<br>equation | $\text{R}^2$<br>Correlation<br>coefficient |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------|-----------------------------------------------|---------------------------------------------------------------|-------------------------------------------------------|---------------------|--------------------------------------------|
| CK                                                                                                                                                      | 10                                                                      | First-order       | 230 ~ 440                                     | 34.55                                                         | 3409.1                                                | $y=-4156.1x-5.8441$ | 0.9937                                     |
|                                                                                                                                                         |                                                                         | Second-order      | 440 ~ 600                                     | 92.49                                                         | 304604211.4                                           | $y=-11125x+4.5716$  | 0.9874                                     |
| CK                                                                                                                                                      | 20                                                                      | First-order       | 230 ~ 440                                     | 36.14                                                         | 4436.2                                                | $y=-4346.7x-5.6256$ | 0.9963                                     |
|                                                                                                                                                         |                                                                         | Second-order      | 440 ~ 600                                     | 72.45                                                         | 9140833.4                                             | $y=-8714x+1.3096$   | 0.9932                                     |
| CK                                                                                                                                                      | 30                                                                      | First-order       | 230 ~ 440                                     | 31.39                                                         | 1252.97                                               | $y=-3775.5x-6.7491$ | 0.9935                                     |
|                                                                                                                                                         |                                                                         | Second-order      | 440 ~ 600                                     | 67.73                                                         | 3654818.4                                             | $y=-8146.8x+0.4602$ | 0.9913                                     |
| RS                                                                                                                                                      | 10                                                                      | First-order       | 230 ~ 440                                     | 29.75                                                         | 989.3                                                 | $y=-3578.9x-6.9318$ | 0.9891                                     |
|                                                                                                                                                         |                                                                         | Second-order      | 440 ~ 600                                     | 32.85                                                         | 3764.3                                                | $y=-3950.7x-5.6943$ | 0.9650                                     |
| RS                                                                                                                                                      | 20                                                                      | First-order       | 230 ~ 440                                     | 34.66                                                         | 3099.7                                                | $y=-4169.6x-5.9425$ | 0.9991                                     |
|                                                                                                                                                         |                                                                         | Second-order      | 440 ~ 600                                     | 39.67                                                         | 12101.2                                               | $y=-4771.8x-4.7154$ | 0.9925                                     |
| RS                                                                                                                                                      | 30                                                                      | First-order       | 230 ~ 440                                     | 31.16                                                         | 1219.4                                                | $y=-3747.4x-6.7687$ | 0.9957                                     |
|                                                                                                                                                         |                                                                         | Second-order      | 440 ~ 600                                     | 39.03                                                         | 10486.1                                               | $y=-4694.4x-4.8423$ | 0.9963                                     |
| Note: the leaves of sweet cherry trees under rain-shelter cultivation are RS, and the leaves of sweet cherry trees under open-field cultivation are CK. |                                                                         |                   |                                               |                                                               |                                                       |                     |                                            |

## Conclusion

The thermolysis of RS and CK leaves was compared. The main decomposition stage was divided into four stages. The pyrolysis rate of sweet cherry leaves is the sum of the pyrolysis rates of hemicellulose, cellulose, lignin and a small amount of inorganic materials. Due to differences in environmental factors under the different cultivation patterns, the contents of hemicellulose, cellulose, and lignin in the CK and RS leaves are also different, and the performance of the main combustion reaction stage is different. The pyrolysis behaviour of sweet cherry leaves in the low temperature region (220 ~ 440 $^{\circ}\text{C}$ ) conforms to the first-order pyrolysis reaction kinetics rule, while the pyrolysis behaviour in the high temperature region (440 ~ 600 $^{\circ}\text{C}$ ) satisfies the second-order reaction kinetics. The research on pyrolysis characteristics and kinetics is of great significance to the application value of bioresources, the construction of an industrialized development system and the improvement of its comprehensive economic benefits. These results provide a theoretical basis for the development and utilization of energy during the pyrolysis of deciduous tree species leaves.

# Declarations

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## Author contributions

H.Z. and Q.L. conceived of and wrote the manuscript. H.Z. and Y.J. conducted data analysis and prepared the figures. H.Z. and Y.L., collected the data. All authors reviewed the manuscript.

## Competing interests

The authors declare no competing interests.

## Statement of compliance

The use of plant material, comply with relevant institutional, national, and international guidelines and legislation.

## Data availability

The datasets used in the current study are available from the corresponding author on reasonable request.

## Additional information

**Correspondence** and requests for materials should be addressed to H.Z.

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## Figures

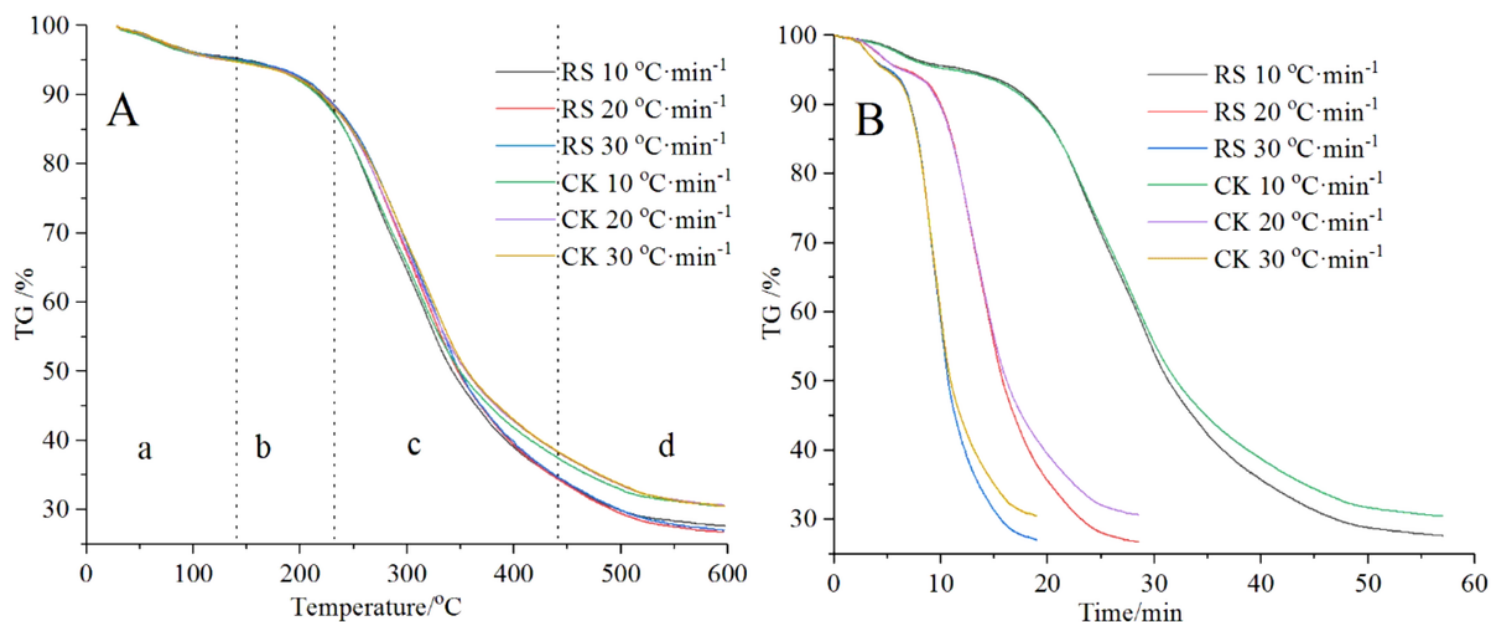


**Figure 1**

TG curves of sweet cherry leaves under different cultivation patterns at different heating rates (A. TG-Temperature, B. TG-Time)

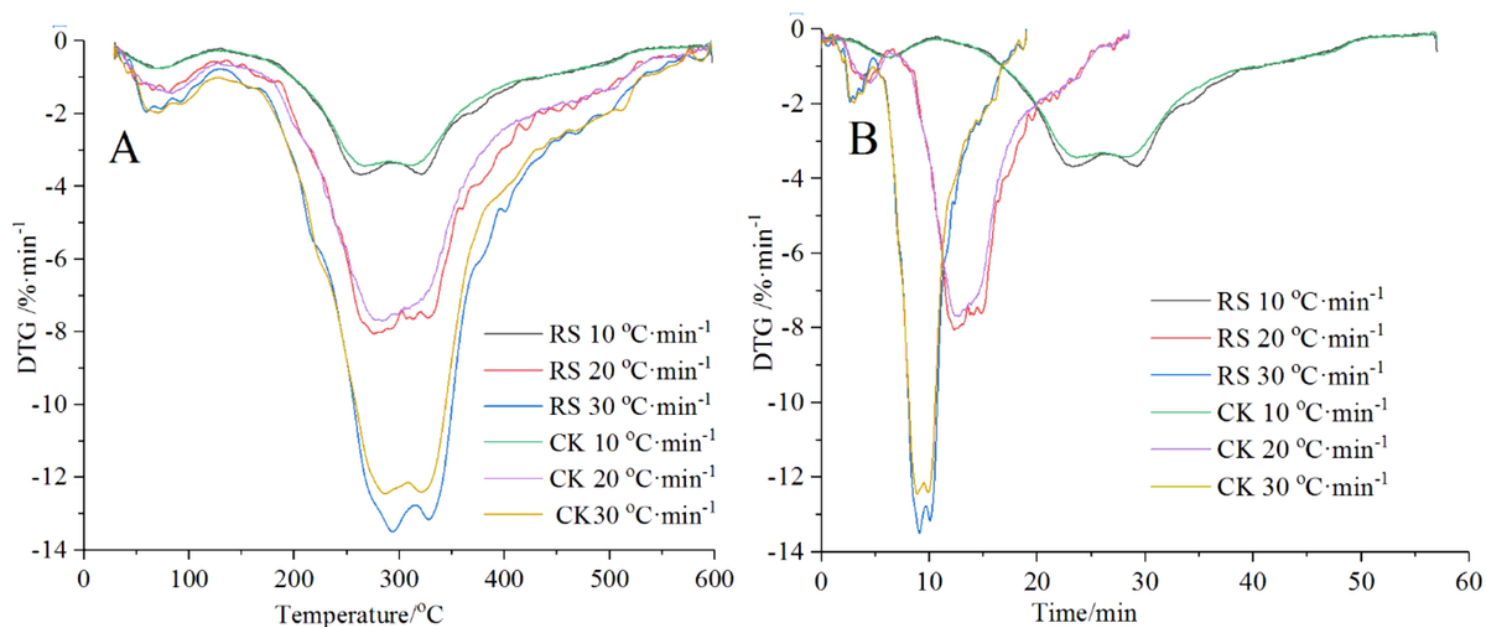


Figure 2

DTG curve of sweet cherry leaves in different cultivation patterns at different heating rates (A. DTG-Temperature, B. DTG-Time)

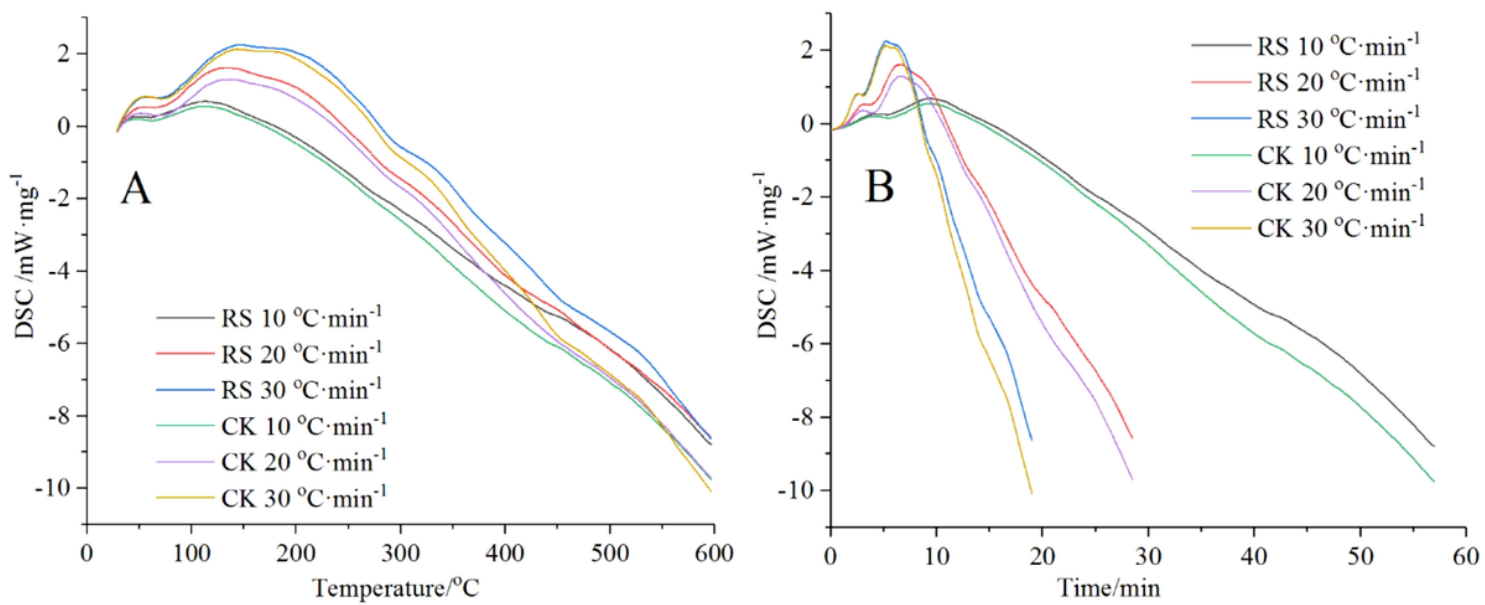


Figure 3

DSC curve of sweet cherry leaves under different cultivation patterns at different heating rates (A. DSC-Temperature, B. DSC-Time)

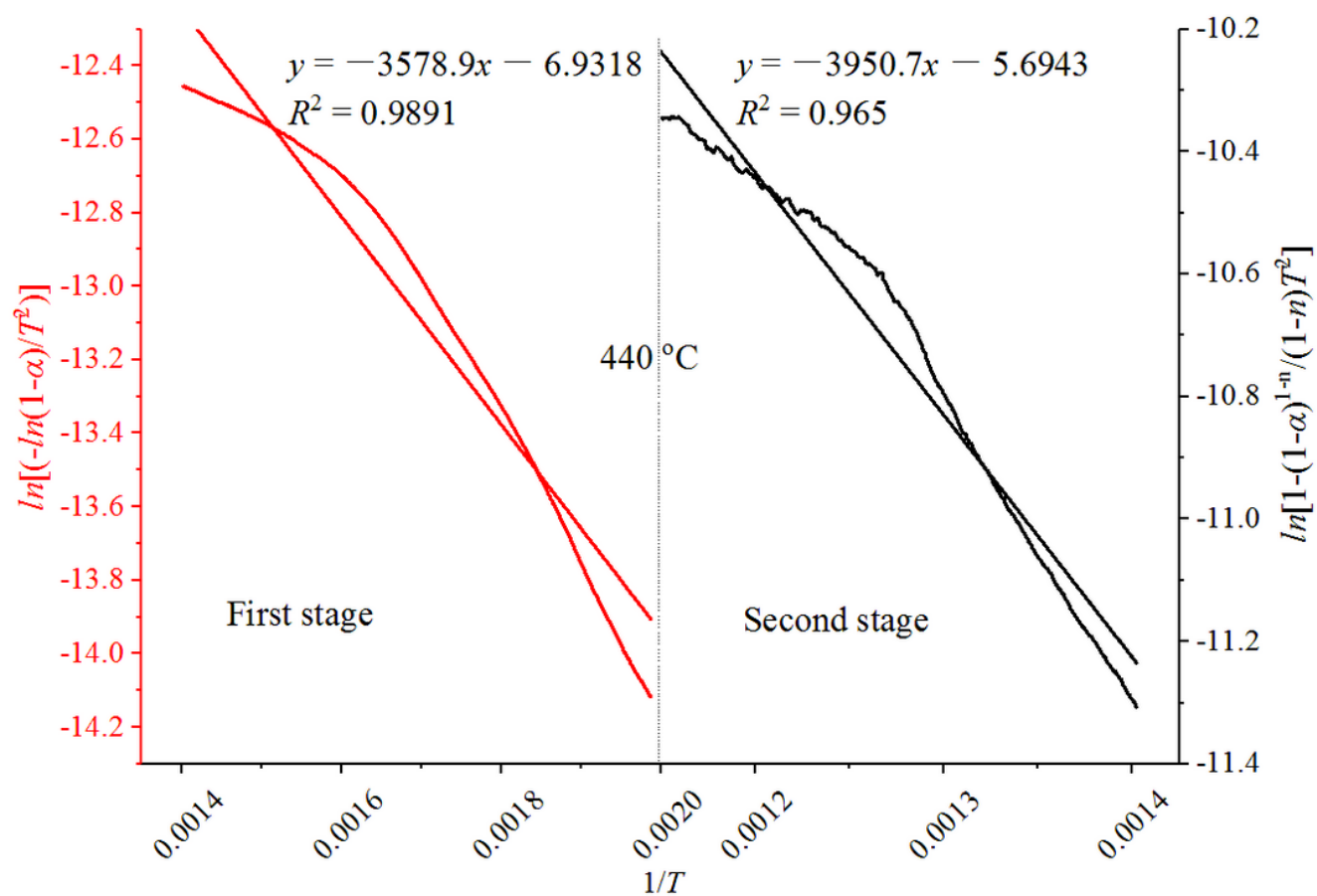


**Figure 4**

Dynamic regression analysis for pyrolysis of leaves of sweet cherry tree under rain-shelter cultivation at  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$