Pyrolysis Characteristics and Kinetics of *Prunus avium* L. Leaves Using Thermogravimetric Analysis

Quan Li,[a,b] Fangzhi Zhu,[a] Fei Shi,[a] Nan Zhang,[a] and Huimin Zhang [a,*]

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) were analysed using thermogravimetry (TG), derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) at three heating rates of 10, 20, and 30 °C·min^{-1}. 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 29.8 to 36.1 kJ·mol^{-1} in the first-order pyrolysis kinetics stage. The second-order pyrolysis kinetics stage can fit the pyrolysis process well. A significant difference was observed in the pyrolysis characteristics or the kinetics between CK and RS, which were related to the heating rate and the hemicellulose content, cellulose content, and lignin ratio in each sample.

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*Contact information: a: School of Civil Engineering and Architecture, Suqian University, Suqian, 223800, China; b: Jiangsu Province Engineering Research Center of Prefabricated Building and Intelligent Construction, Suqian University, Suqian, 223800, China; *Correspondence: mhz722@126.com*

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 (Foo and Hameed 2009). Biomass energy, as an efficient and renewable natural resource, is an alternative energy source with great development potential (Liu and Wu 2013). 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 biomass sources (Yagmur 2012; Gil *et al*. 2013).

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.* (2018) investigated the pyrolysis characteristics of moso bamboo (*Phyllostachys pubescens*), including the outer layer, middle layer, inner layer, and leaves, through thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR) and pyrolysis–gas chromatography–mass spectrometry (Py-GC/MS). Their results showed that 70% of the mass loss occurred at the rapid pyrolysis stage at temperature range of 200 to 400 °C. It can be found from the above studies that most scholars typically used the biomass pyrolysis properties of materials by differential thermal analysis (DTA) (Francisco-Fernández *et al.* 2015).

Some researchers have performed research on pyrolysis process parameters (Grønli *et al.* 2002; Zhou *et al.* 2013). Li *et al.* (2016) revealed the decay resistance and physico-chemical behaviour during the heating process of *C. camphora* methanol extracts by analysing the pyrolysis characteristics and kinetic analysis of sapwood brown rot of *P. Massoniana* treated with *C. camphora* methanol extracts. These studies have often focused on the change in the pyrolysis characteristics of various biomass materials, but there has been no research comparing the pyrolysis performance of plants under different cultivation patterns. This study contributes to the knowledge of the ability to utilize *Prunus avium* L. leaves for pyrolysis characteristics, such as kinetics analysis, *via* a thermogravimetric analyzer.

Trees produce a large amount of leaves, which can be used as a biomass energy source. The waste after combustion (such as water and carbon dioxide) has little impact on the environment. Choosing mountainous areas with abundant forests, rural areas, and urban parks where trees produce a large amount of fallen leaves can reduce energy transmission losses and system investment costs. In addition, making bioenergy from fallen leaves can reduce dependence on the import of fossil energy such as coal, natural gas and oil, thus ensuring the national energy security.

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) (Dziadek *et al.* 2018; Gyeviki *et al.* 2019). 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 (Park *et al.* 2009; Hosseini *et al.* 2018). 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). Rain-shelter cultivation is an important cultivation approach that has been widely applied to fruit tree in rainy regions. Transparent plastic films are normally used to cover the roof during sweet cherry development stages, preventing rainfall damage and eliminating fruit disease incidences (Polat *et al*. 2005). The pyrolysis of sweet cherry leaves is a process involving complex thermophysical and chemical changes. The analysis and evaluation of the thermal stability, thermodynamics parameters, 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.

EXPERIMENTAL

Plant Material and Experimental Base

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 in July 2019. The rain-shelter facilities were 4 span rain-shelters built in April 2014. The management techniques for sweet cherry trees in orchards under rain-shelter cultivation or under open-field cultivation were consistent. If encountering drought, it is necessary to fertilize and irrigate the fruit trees (Gao *et al*. 2016). 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 the authors’ laboratory. The main chemical components in the leaves of sweet cherry are hemicellulose, cellulose, and lignin. The proportion of the three main components in the leaves of sweet cherry under different cultivation patterns was different. Three trees with normal growth and relatively consistent growth potential were selected randomly from rain-shelter cultivation (RS) and open field cultivation (CK), 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 min and then dried at 80 °C to constant weight. The dried leaves were ground with a mini-pulveriser, and 40 to 60 mesh powder was screened as the raw material for the test.

Thermogravimetric Analysis

The experiments were conducted using a Thermogravimetry-differential scanning calorimetric (TG-DSC) analyser (NETZSCH STA449F5, Berlin, Germany). The samples were purged with N_2 at heating rates of 10, 20, and 30 $°C \cdot min^{-1}$. The samples’ mass used was 8 mg, and three biological repeats were done for each sample. Eighteen groups of samples in total were heated from 30 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 (OriginLab, Origin 9.4, Northampton, MA, USA).

RESULTS AND DISCUSSION

Pyrolysis Characteristics

The pyrolysis characteristics of sweet cherry leaves are shown in Figs. 1 to 3. It can be concluded that the RS samples had 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_2 gas protection at full temperature can be divided into four stages (Figs. 1 (A) a, b, c, d) (Domínguez *et al*. 2008; Lu *et al*. 2011). 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 loss accounted for approximately 5% of the total mass loss, which was 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 at this stage was approximately 140 to 220 °C), and the TG curve did not decrease much. The mass loss rate at this stage was approximately 5%. The main reason is that the unstable hemicelluloses in the leaves begin to pyrolyze, generating a small amount of CO, CO_2, H_2, and other gases, and a small amount of depolymerization, internal recombination, and ‘glass transition’ occur (Yang *et al*. 2010; Khelfa *et al*. 2013). The third stage is the pyrolysis stage (the temperature range is approximately 220 to 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 dropped sharply at this stage by approximately 50 to 55%. The rapid degradation of cellulose and hemicellulose generates a large amount of volatiles and small molecule gas products such as CO, CO_2, CH_4, and H_2. The fourth stage is the carbonization stage (temperature > 440 °C), and the TG curve at this time was relatively stable compared with the third stage. The mass loss at this stage was relatively small, approximately 7% (Goyal *et al*. 2008; Sun *et al*. 2017). The amount of solids remaining at 600 °C was about 30% in each case, indicating the presence of a certain amount of crude fat, crude protein, and a small amount of relatively stable minerals (such as inorganic salts) in the leaves. These substances are resistant to high temperatures and usually gradually degrade under high temperature conditions exceeding 600 °C.

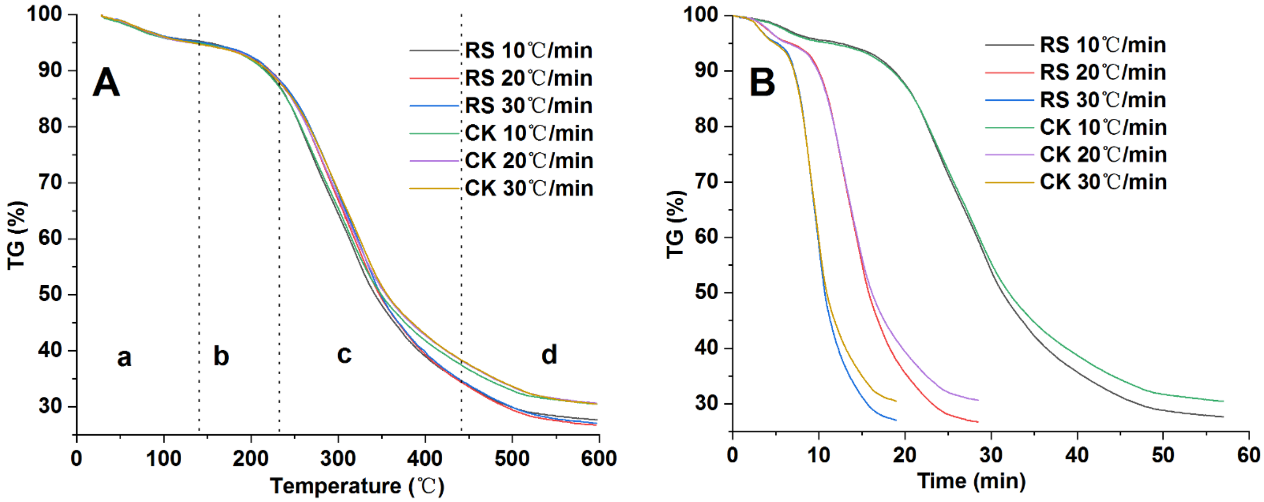

Fig. 1. TG curves of sweet cherry leaves under different cultivation patterns at different heating rates (A. TG-Temperature, B. TG-Time)

The TG curves reflect the relationship between the sample mass, temperature, and heating rate (Zhang *et al*. 2018; Ornaghi *et al*. 2019). As can be 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 present in the RS leaves are higher than that in the CK leaves (Zhang *et al*. 2021). 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) (Aiman and Stubington 1993; Yang *et al*. 2006). In Fig. 2, the derivative thermogravimetry (DTG) curve peak clearly presents three gradients, with the peaks from large to small in the order 30 °C·min^{-1} > 20 °C·min^{-1} > 10 °C·min^{-1}.

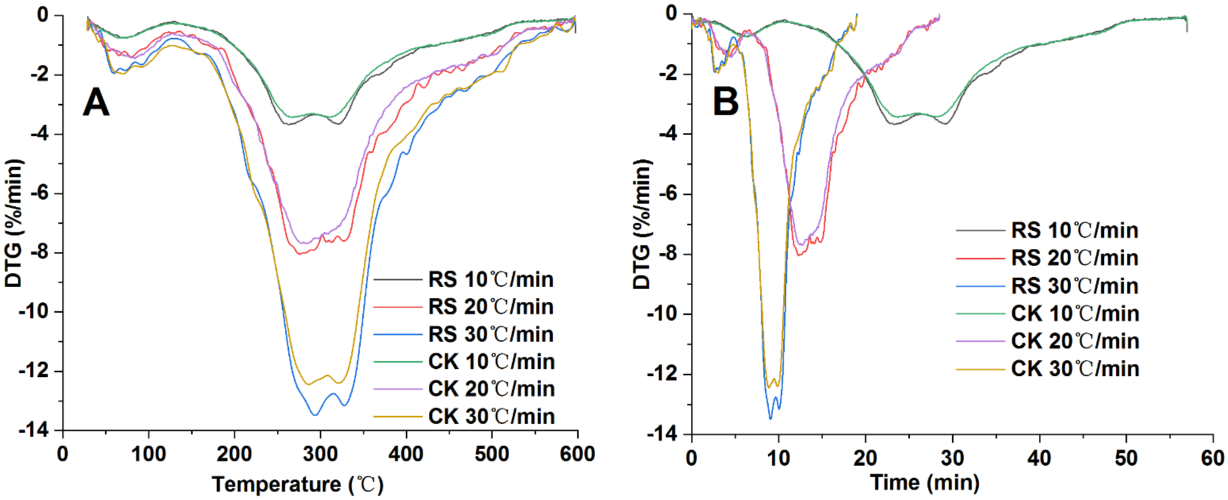

Fig. 2. DTG curve of sweet cherry leaves in different cultivation patterns at different heating rates (A: DTG-Temperature, and B: DTG-Time)

Under the same heating rate, the DTG of the RS leaves was slightly higher than that of the CK leaves. As the heating rate increased, the rate of change of its mass with temperature and time also increased. The two samples exhibited 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 to 180 °C, which may be due to the precipitation of some volatile oils at lower temperatures. At stage C (220 to 440 °C), the slope of the sample mass loss curve and the corresponding DTG-T (DTG and temperature) values gradually increased, which can be attributed primarily to the conversion of cellulose, hemicellulose, and lignin, the main components of leaves, into small molecular volatile substances (Ren *et al*. 2013). The DTG obviously underwent a severe pyrolysis reaction at approximately 280 and 330 °C. Two distinct downward peaks appeared at these two positions, and the peak sizes were different. This outcome was primarily due to the pyrolysis of sweet cherry leaves that occurs in two stages: the former peak indicates that the pyrolysis of hemicellulose had basically ended and the pyrolysis reaction of lignin had not yet reached the maximum (Ahmad *et al*. 2018). The latter peak indicates that the pyrolysis reaction of cellulose had 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 (Zhao *et al*. 2018). If the hemicellulose content is significantly lower than the cellulose content, the two dispersed wave peaks will form a wide wave peak (Shen and Gu 2009). The two peaks formed here illustrate the small difference in cellulose and hemicellulose contents in the leaves. After 440 °C, as the temperature continued to increase, the mass loss rate decreased rapidly, and the TG and T in the TG-T (TG and temperature) curve had an approximately linear relationship. At this stage, the pyrolysis reaction of the lignin continued, and the DSC curve continued to fall. This outcome shows that there was a certain amount of crude fat and crude protein present in the sweet cherry leaves that can only be thermally degraded at high temperatures (Di Blasi 2008; Patwardhan *et al*. 2009). The pyrolysis process of biomass materials in these four stages can be analyzed and confirmed through various experimental equipment and methods. In addition to using a thermogravimetric analyzer, instruments such as gas chromatographs and mass spectrometers can also be used to qualitatively and quantitatively analyze the gases released during the pyrolysis of biomass materials (Li *et al.* 2021; Yuet *et al*. 2022). Based on mass spectrometric analysis of woody biomass, Penzik *et al*. (2022) stated that, in the composition of pyrolytic gases, H_2O and CH_4, have a greater contribution and CH_4, CH_3COOH, furans, phenols, and aromatic compounds are present to a lesser extent. In addition, the TG/FT-IR techniques, UV-spectroscopy, microwave extraction, XRD and SEM can further analyze the composition and structure of solid samples to verify the four stages of pyrolysis process (Bielecki *et al*. 2022).

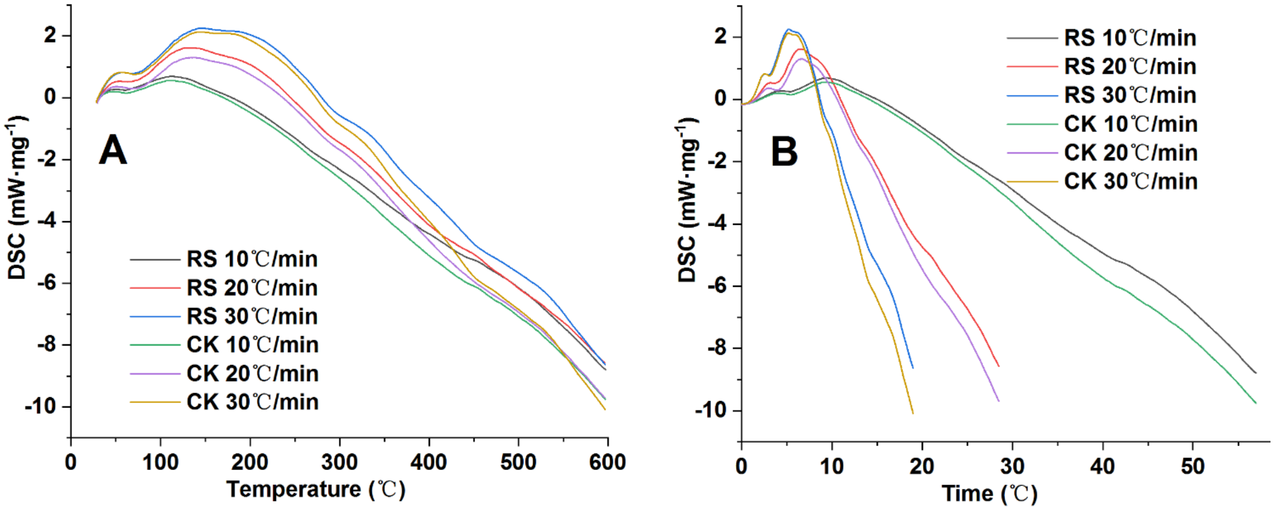

Fig. 3. DSC curve of sweet cherry leaves under different cultivation patterns at different heating rates (A: DSC-Temperature and B: DSC-Time)

Figure 3(A) shows that each sample mainly absorbed heat before reaching 140 °C. Above 140 °C, the DSC curve gradually became negative, and thermal decomposition of the pyrolysis stage of holocellulose (cellulose and hemicellulose) and the pyrolysis stage of lignin began. The DSC curve trend was relatively flat in the range 140 to 220 °C. Hemicellulose began to pyrolyze, but the activation energy was not high. The DSC curve decreased rapidly at 220 to 440 °C, primarily due to the rapid pyrolysis of hemicellulose, cellulose, and lignin. Figure 3(B) shows that under the same temperature rising condition, the heat absorbed by the CK leaves was 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 were different in hemicellulose, cellulose, and lignin contents.

Modelling of Pyrolysis Kinetics

The mass loss of the sample (in TG) and the changes in heat flux (in 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 (solid) → B (solid) + C (gas)

The reaction mechanism function is calculated using the Coats-Redfern equation and the thermal analysis kinetic triplet comparative law (Wadhwani *et al*. 2017):

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

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

Let plot $\ln[\frac{-\ln(1-\alpha)}{T^2}]$ with $\frac{1}{T}$ when n = 1, $\ln[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}]$ plot with $\frac{1}{T}$ when $n \neq 1$, and it is then possible to 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. Here the parameter α denotes the extent of reaction, $\alpha = \frac{W_0 - W_t}{W_0 - W_\infty}$, Heating rate $\beta = \frac{dT}{dt}$ is a constant, *t* is the reaction time (min), W_0 denotes quantity before mass loss (mg), W_∞ is residue quantity (mg), W_t is weight at the beginning of *t* (mg), *Z* is pre-exponential factor (min^{-1}), *E* denotes activation energy ($kJ \cdot mol^{-1}$), *R* is universal gas constant (8.314×10^{-3} $kJ \cdot K^{-1} \cdot mol^{-1}$), and *T* is reaction temperature (K).

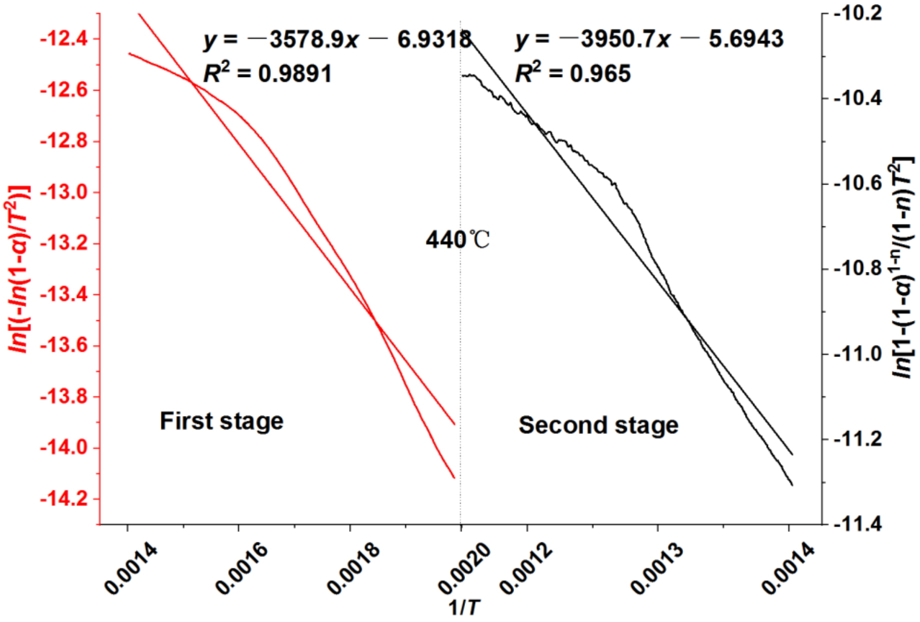

Fig. 4. Dynamic regression analysis for pyrolysis of leaves of sweet cherry tree under rain-shelter cultivation at 10 °C·min^{-1}

The theoretical analysis of biomass pyrolysis characteristics is mainly based on the analysis of kinetic processes centred on a single-component reaction model or a multicomponent parallel reaction model. Through the calculation of the experimental data, it was 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 to 440 °C) is consistent with the first-order pyrolysis kinetic rule, and the pyrolysis behaviour in the high temperature region (440 to 600 °C) meets the second-order reaction kinetic rule (Fig. 4) (Cui and Kuo 2013). 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.

Table 1. Thermodynamic Parameters of Different Reaction Stages with the Coats-Redfern Method

Samples	β Heating Rate (°C·min^{-1})	Reaction Stage	T Temp. Range (°C)	E Activation Energy (KJ·mol^{-1})	A Pre-exponential Factor (min^{-1})	Fitting Equation	R^2 Coefficient of Determination
CK	10	First-order	230 to 440	34.55	3409.1	y = -4156.1x - 5.8441	0.9937
		Second-order	440 to600	92.49	304604211.4	y = 11125x + 4.5716	0.9874
CK	20	First-order	230 to 440	36.14	4436.2	Y = -4346.7x - 5.6256	0.9963
		Second-order	440 to 600	72.45	9140833.4	y = 8714x + 1.3096	0.9932
CK	30	First-order	230 to 440	31.39	1252.97	Y = -3775.5x - 6.7491	0.9935
		Second-order	440 to 600	67.73	3654818.4	y = 8146.8x + 0.4602	0.9913
RS	10	First-order	230 to 440	29.75	989.3	y = -3578.9x - 6.9318	0.9891
		Second-order	440 to 600	32.85	3764.3	y = -3950.7x - 5.6943	0.9650
RS	20	First-order	230 to 440	34.66	3099.7	y = -4169.6x - 5.9425	0.9991
		Second-order	440 to 600	39.67	12101.2	y = -4771.8x - 4.7154	0.9925
RS	30	First-order	230 to 440	31.16	1219.4	y = -3747.4x - 6.7687	0.9957
		Second-order	440 to 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

Analysis of the Kinetics of Pyrolysis

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) obtained were all above 0.98, and good linear fitting effect was achieved. In the first-order pyrolysis reaction stage, the activation energy was 29.75 to 36.14 kJ·mol^{-1}, with little difference. This stage mainly involves the pyrolysis of hemicellulose and cellulose. Its activation energy is small compared to the hemicellulose thermogravimetric test results (48.5 to 88.4 kJ·mol^{-1}) obtained by Orfão *et al*. (1999). This outcome may be because of 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 was 32.85 to 92.49 kJ·mol^{-1} and mainly involved the pyrolysis of lignin, a small amount of organic extracts (such as crude protein, *etc*.), minerals (inorganic salts, *etc*.), and other chemically stable substances (Hu *et al*. 2016; Pérez *et al*. 2018), and the specific results are shown in Table 1. Sweet cherry leaves under different cultivation patterns were heated at three heating rates, and the activation energy *E* in the second-order pyrolysis reaction stage was 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, which has higher thermal stability, while the first stage mainly involved the pyrolysis of hemicellulose and cellulose with relatively unstable structures (Navarro *et al*. 2018). Therefore, the activation energy in the first-order pyrolysis reaction stage was 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 were similar to those of wood. Although the management techniques of sweet cherry trees under different cultivation patterns were the same, there were differences in light and climatic environmental factors, and the hemicellulose, cellulose and lignin contents in CK and RS leaves were also different. So the pyrolysis characteristics and kinetic parameters of the leaves were related to open or shelter growing conditions of sweet cherry tree. Compared with the RS leaves, the activation energy of the CK leaves was slightly higher, indicating that the CK leaves had more stable chemical properties, showed good thermal stability, and were not as easy to pyrolyze.

CONCLUSIONS

The thermolysis of RS and CK leaves was compared in this study.

1. The main decomposition stage was divided into four stages. The net pyrolysis 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 were also different, and thus the performance of the main combustion reaction stage was different.
2. RS receives less light and higher environmental temperature, resulting in a higher relative content of cellulose in leaves, leading to a higher pyrolysis reaction rate. However, CK receives more light and lower environmental temperature, resulting in a higher relative content of lignin in leaves, resulting in a lower pyrolysis reaction rate.
3. The pyrolysis behaviour of sweet cherry leaves in the low temperature region (220 to 440 °C) conformed to the first-order pyrolysis reaction kinetics rule, while the pyrolysis behaviour in the high temperature region (440 to 600 °C) satisfied 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.

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Declarations

Competing interests

The authors declare no competing interests.

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