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Effects of heating rate on fast pyrolysis behavior and product distribution of Jerusalem artichoke stalk by using TG-FTIR and Py-GC/MS

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A B S T R A C T

In this work, the effects of heating rate on fast pyrolysis behavior and product distribution of Jerusalem artichoke stalk (JAS) were investigated fist by TG-FTIR (heating rates: 20, 30, 50, 100, 300, 500 °C/min) and then via Py-GC/MS (heating rates: 100, 1000, 5000 10000 °C/s). The results showed that with the heating rate increased, TG and DTG curves obviously shifted toward the high-temperature range, and the number of peaks in DTG curves reduced from three to two. The model-free method indicated that the apparent activation energy of JAS pyrolysis was 286 kJ/mol at the low heating rate and increased to 351 kJ/mol at the high heating rate. The distributed activation energy model showed that the value of pre-exponential factor increased with the heating rate increased and the kinetic compensation effect was obvious during the conversion from 0.3 to 0.7. Total 44 compounds were identified by GC/MS. Acid, phenol and carbonyl compounds were the major products groups. With the heating rate increased, the relative contents of acid increased whereas the relative contents of phenolic substance decreased. The yield of carbonyl compounds was maximum at the heating rate of 5000 °C/s.

1. Introduction

Jerusalem artichoke (JA, Helianthus Tuberosus L.), also known as sunchoke, is originally from North American and it is one of the crops taken from the New World and Asia [1]. JA is seriously tolerant of environmental stresses, such as drought and salinity. In the saline land of China, this drought-resistant and salinity-tolerant vegetation has been widely planted to improve the soil and water conservation [2]. The major components of JA are tuber (JAT) and stalk (JAS). JAT has been explored for making inulin and liquid chemical products [3], but little attention has been paid to how to utilize JAS efficiently and cleanly [4].

For a long period, a large number of agricultural residues in developing countries have been burned directly for cooking and space heating, causing serious pollution and waste of resources [5]. Agricultural residues such as JAS, as an important biomass material, can be converted into bio-fuels and value-added chemical products [6]. Pyrolysis of biomass, which can produce gaseous, liquid and solid products simultaneously, is considered the most potential method for biomass thermochemical conversion [7]. Therefore, investigating the pyrolysis properties of JAS is of great help to make JAS as a bio-energy resource. Sun et al. studied JAS pyrolysis characteristics and kinetics through thermogravimetric analysis method at heating rates of 5, 10, 20 and 30 °C/min and pyrolysis temperature range of 50–800 °C. The results showed that the pyrolysis of JAS included three stages and the main pyrolysis occurred in the second stage. The temperature range of JAS thermal decomposition was 200–400 °C and over 75% weight was degraded. The apparent activation energy of JAS pyrolysis calculated from TG data was 270 kJ/mol [8]. Fast pyrolysis of biomass is a fundamental thermochemical conversion process with both ecological and industrial importance [9]. In fast pyrolysis reactors, a rapid heating rate is employed to maximize the production of liquid and minimize the yield of bio-char [10]. However, previous researchers have not studied characteristics and kinetics of JAS fast pyrolysis in much detail.

An understanding of biomass pyrolysis kinetics, characteristics and product distribution are imperative for the design and operation of industrial biomass conversion systems. Thermogravimetric analysis (TG) coupled with Fourier Transform Infrared (FTIR) analysis has been widely used to study biomass thermal

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decomposition characteristics, kinetics and evolved products [11–13]. Besides TG-FTIR, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is another important technique to study biomass pyrolysis. The pyrolyzer can provide different pyrolysis conditions, while the GC/MS can separate and identify complex volatile products precisely [14,15]. It is an important method to investigate the thermal behavior of biomass by combining TG-FTIR and Py-GC/MS, however, studies by combining these two methods still remain few [16].

Previous researchers have achieved significant advances in comprehending the effects of heating rates on biomass pyrolysis [17,18]. Ozbay et al. studied the influence of heating rate on cottonseed cake pyrolysis by a fixed bed reactor and found that with the heating rate increasing, the yield of bio-oil was moderately increased [19]. Salehiet et al. have reported that the bio-oil yield increased by 8% when the heating rate of sawdust increased from 500 °C/min to 800 °C/min, but when the heating rate further increased, there was no significant change in bio-oil production [20]. Nevertheless, traditional pyrolysis experiments of biomass took place in a TG analysis system typically with a heating rate less than 50 °C/min [21]. The pyrolysis behavior and product distribution of JAS, especially the effects of heating rate on these fields at high heating rates, have not been fully researched. Therefore, in this work, pyrolysis experiments were performed by using TG-FTIR and Py-GC/MS at different heating rates. At the same time, the thermal behavior, kinetics and product distribution of JAS were also analyzed to obtain more useful information of JAS fast pyrolysis.

The objectives of this work are to determine the effects of heating rate on fast pyrolysis behavior, kinetic parameters and product distribution of JAS. For these purposes, the TG data of JAS pyrolysis at different heating rates were collected, and the apparent activation energy of decomposition was calculated by Friedman method, Flynn-Wall-Ozaw method and Kissinger-Akahira-Sunose method. The effects of heating rate on fast pyrolysis product distribution were also evaluated by Py-GC/MS. The results of this work can provide a theoretical basis for JAS utilization and offer helpful information for design and optimization of JAS pyrolysis system.

2. Material and methods

2.1. Raw material

JAS, collected from the experimental field of Yantai Institute of Coastal Zone Research of Chinese Academy of Sciences in Shandong province, was used as raw material in this experiment. Before the test, the sample was screened into a particle size of 40 mesh and dried in vacuum oven at 80 °C for 10 h in order to remove the free moisture. The proximate analysis of JAS was measured by the method of Chinese National Standards GB/T212-2008, which could obtain the content of volatile matter (VM), fixed carbon (FC) and ash. The ultimate analysis of JAS was conducted by an Elemental analyzer (EA3000, ELEMENTAR Company, Germany) to determine the content of carbon, hydrogen, sulfur, nitrogen and oxygen. The data of proximate analysis and ultimate analysis were obtained on a dry basis (db) and the contents of fixed carbon and oxygen were calculated by difference. JA is usually planted in saline land and thus some of alkali and alkaline earth metals (AAEMs) may be concentrated in JAS. The emission of AAEMs (mainly K^+, Na^+, Ca^{2+} and Mg^{2+}) during the pyrolysis can catalyze the reaction and further change the pyrolysis process [22,23]. To investigate the effect of AAEMs emission on pyrolysis at different heating rate, the content of K^+, Na^+, Ca^{2+} and Mg^{2+} of JAS was detected by inductively coupled plasma mass spectrometry (ICP-MS, 2030, Shimadzu Company, Japan). The results of proximate analysis, ultimate analysis, ICP-MS and Van Soest [24] of JAS were shown in Table 1.

2.2. TG-FTIR analysis

Thermogravimetric analysis (TG) is a technique commonly used to determine the kinetic parameters of pyrolysis. In this work, TG analysis of JAS was performed by a thermogravimetric analyzer (STA 449F3 NETZSCH Company, Germany) with a high-speed heating furnace (NETZSCH Company, Germany). The high-speed heating furnace is a special furnace which can provide a heating rate range from 0 to 1000 °C/min and a maximum temperature of 1250 °C. For each experiment, about 5 mg of pre-dried sample was heated and the flow rate of carries gas (ultrahigh purity N_2, >99.999%) was set at 100 ml/min. In order to evaluate the effect of heating rate on pyrolysis behavior and activation energy, the raw material was heated from 30 °C to 900 °C at the heating rate of 20 °C/min, 30 °C/min, 50 °C/min, 100 °C/min, 300 °C/min and 500 °C/min, respectively. All experiments were repeated at least three times at each heating rate until the deviation of mass loss was lower than 1%, and the average of the three closest experimental results was used to plot the TG curves. The gaseous products released during the pyrolysis were monitored online by a Fourier-transform infrared spectrometer (FTIR TENSORII, BRUKER Company, USA) coupled with TG. The transfer line used to connect TG with FTIR was a 1 m long Teflon tube with an internal diameter of 2 mm. The temperature of transfer line was heated to 200 °C to reduce the probability of gases condensation. The spectra were collected at a resolution of 4 cm^{-1} over the range of 4000–500 cm^{-1} and the spectrum scan frequency was 32 times per minute.

2.3. Py-GC/MS analysis

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) system was employed in this study to separate and identify the pyrolysis products at different heating rates. For this purpose, a Pyroprobe 5000 (CDS Company, USA) was directly coupled to a gas chromatography/mass spectrometry (436-GC/SQ-MS, Tianmei Company, China). About 0.3 mg sample was placed in a quartz tube (2.5 cm × 2 mm) and the quartz tube was surrounded by a platinum wire in probe. The platinum wire was heated from room temperature to 600 °C at different heating rates. The residence time of samples was 10s. In industrial production process of fast pyrolysis or flash pyrolysis, the sample was rapidly heated to reaction temperature within a few milliseconds. To simulate this process, the heating rates of pyrolysis were set at 100 °C/s, 1000 °C/s, 5000 °C/s and 10000 °C/s, respectively. The chromatographic separation of volatile products was performed using an Agilent DB-5MS capillary quartz column (60 m × 0.25 mm, 0.25 μm, USA). Helium was used as carrier gas at a constant flow rate of 1.0 ml/min. Before the separation, the temperature of the chromatographic column was progressively increased as follows: (i) 40 °C for 3 min, (ii) from 40 °C to 180 °C at a heating rate of 4 °C/min, (iii) from 180 °C to 280 °C at a heating rate of 5 °C/min, (iv) from 280 °C to 300 °C at a heating rate of 8 °C/min and holding 5 min.

2.4. Kinetic methods

The kinetic parameters of JAS pyrolysis can be calculated based on TG data. The thermal decomposition of biomass proceeds via a complex set of concurrent and competitive reactions, and the mechanism for biomass pyrolysis remains a mystery. Model-free methods, such as Friedman method, Flynn-Wall-Ozawa (FWO) method and Kissinger-Akahira-Sunose (KAS) method, are commonly used methods to determine activation energy due to the more reliable E_a can be obtained by such model without any mechanism assumptions [25,26]. However, model-free methods