Journal of Analytical and Applied Pyrolysis 120 (2016) 330–333

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Study on pyrolysis characteristics of red pepper stalks to analyze the changes of pyrolytic behaviors from xylophyta to herbage

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ARTICLE INFO

Article history:
Received 4 May 2016
Received in revised form 30 May 2016
Accepted 30 May 2016
Available online 31 May 2016

Keyword:
Pyrolysis
Red pepper stalks
Py-GC/MS
TGA
Biomass

ABSTRACT

To explore the changes of pyrolysis behaviors from xylophyta to herbage, pyrolysis properties of red pepper stalks (RPS) as a representative kind of biomass of high lignin content of agricultural residues were studied by using TGA and Py-GC/MS. The results indicated that contents of cellulose, 43.2 wt.%, and of lignin, 24.7 wt.% were higher than those of corn stalks, wheat stalks and cotton stalks, but closer to those of the poplar wood. The pyrolysis process mainly occurred in three stages, and with an increasing heating rate from 10 °C/min to 30 °C/min, the TGA curves shifted to a lower temperature. With an increase in pyrolysis temperature, the contents of sugars, phenols and furans decreased from 3.96%, 13.54% and 10.13% to 1.09%, 7.13% and 1.65%, respectively. The contents of hydroxyacetaldehyde and acetone reached a maximum 13.71% and 20.05% at 500 °C. At 300 °C levoglucose, pentanal and methyl furan content reached maxima of 3.63%, 13.09% and 7.49%, respectively. Different chemical components could account for the changes of pyrolytic behaviors from xylophyta to herbage.

1. Introduction

The increasing use of fossil fuels leads to the global environment and energy problems including greenhouse gases, environment pollution, energy crisis and so on, which has pushed human to seek for renewable energy such as solar power, wind power and biomass. As the biomass is abundant, wild-spread and renewable, it has been given considerable attentions in the past decades. Pyrolysis is a thermo-chemical decomposition of organic materials at elevated temperatures in the absence of oxygen (or any halogen), which has been a focus of intensive research on biomass technology in recent years.

Results of pyrolysis behaviors between agricultural residues, such as corn stalks (CS) [1,2], wheat straw (WS) [3,4], cotton stalks (CtS) [5], tobacco residues [6] *etc.*) and wood residues (such as poplar wood (PW) [7], grape residues [8], mallee wood [9] *etc.*), had indicated that the differences existed apparently. It is known that biomass mainly consists of extractives, lignin, cellulose, hemicelluloses and minerals, which vary in relative abundance in the polymer, depending on plant species. The chemical inhomogeneity has important effects on the pyrolysis behaviors [10–12]. On the other hand, physical structures of biomass are also diverse among different kinds of biomass, even fractions of biomass, which affect the transfer of heat and mass in pyrolysis process and result in the difference of pyrolysis behaviors. Therefore, it is necessary to study the individual pyrolysis behaviors of biomass for their optimum applications. In our previous study, the pyrolysis behaviors of sweet potato vines as a representative biomass of low lignin content and high extractives content in agricultural residues was studied [13]. The results indicated its distinctive pyrolysis characteristics.

Red pepper is an important condiment in some counties, especially in China. As a byproducts, red pepper stalks (RPS) was usually discarded, which caused waste of energy and environment pollution. In fact, compared with other agricultural residues such as corn stalks, wheat straw and corn cobs, the lignification degree of RPS is higher, which suggests different pyrolysis characteristics. However, to the best of our knowledge, up to now, no study has been reported about RPS pyrolysis. In this paper, chemical constitutes of RPS were analyzed, and its pyrolysis behaviors were studied by means of TGA and Py-GC/MS.

2. Materials and methods

2.1. Materials and analysis

RPS was collected in 2014 from a local farm in a Beijing suburb in China dried in the sun and stored in plastic bags. Leaves of RPS were removed while the turnks and branches were used for

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http://dx.doi.org/10.1016/j.jaap.2016.05.020

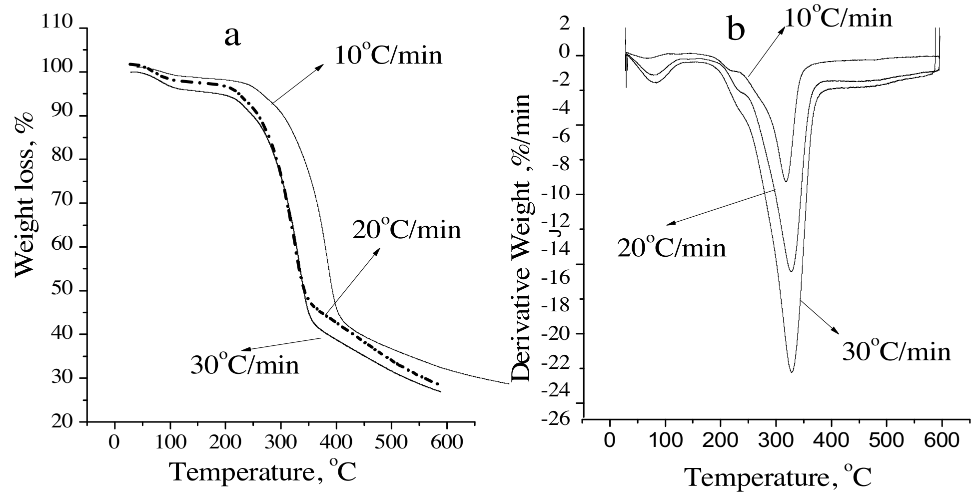

Fig. 1. TGA and DTG curves of RPS at different heating rates.

Table 1
Proximate analysis and chemical components of RPS.

Samples	Proximate analysis, wt.%				Component analysis, wt.%		
	moisture	ash	volatiles	fixed carbon	cellulose	hemicelluloses	lignin
RPS	3.21	4.9	73.9	18.0	43.2	15.8	24.7
CS[a]	3.4	9.6	69.0	18.0	41.0	21.0	16.0
WS[b]	8	8.5	73.0	10.5	34.6	24.5	16.0
CtS[c]	–	–	–	–	32.0	14.4	24.5
PW[d]	9.6	3.7	75.5	11.2	44.8	16.7	30.7

[a] Wang et al. [2].
[b] Habets et al. [4].
[c] Huang et al. [5].
[d] Gu et al. [7].

the experiments. The samples were milled and only the fractions under 20 meshes were used for analysis. The proximate analysis and chemical components of RPS were analyzed according to GB/T 28731-2012 and ASTM E1758-01 respectively.

2.2. TGA

A Thermo-Gravimetric Analyzer (TGA, Perkin Elmer STA 6000, UAS) was used in conducting the pyrolysis experiments of RPS from 30 °C to 600 °C at a heating rate of 10 °C/min, 20 °C/min and 30 °C/min in the nitrogen environment (99.999%) at a flow rate of 50 mL/min.

2.3. Py-GC/MS analysis

A CDS Pyroprobe 5200HP pyrolyzer (Chemical Data Systems) connected with a GC/MS (Perkin Elmer, Clarus 560) was used to conduct the fast pyrolysis tests of RPS. In our experiments, 0.3 mg of the sample was filled in a pyrolysis tube and then pyrolyzed at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C for 20 s with a heating rate of 20 °C/ms, respectively. The rest of experiments and data analyses procedures were all the same as previously reported [14].

3. Results and discussions

3.1. Properties of RPS

Table 1 presents the results of the proximate analysis and component analysis of RPS. The proportions of ash, volatiles and fixed carbon were 4.9 wt.%, 71.9 wt.% and 20.0 wt.%, respectively. The composition ratio of its cell wall was: cellulose 43.2 wt.%, hemicelluloses 15.8 wt.% and lignin 24.7 wt.%.

To illustrate the distinctive chemical compositions of RPS compared to other agriculture residues, the data of other four kinds of biomass including CS [2], WS [4], CtS [5] and PW [7] were cited from the existing literatures. The chemical compositions of CS, WS, CtS and PW had been analyzed by researchers from different countries. However, some factors such as species, locality of growth and methods of test resulted in quite differences among the researchers. Therefore, only modern data were chosen and listed in Table 1. The proportion of ash in RPS was 4.9 wt.%, which was lower than that of CS, 9.6 wt.% and that of WS, 8.5 wt.%,while it was close to that of PW, 3.7 wt.%. This suggested less metal and silicon contents in RPS cell wall than in other crop plants. The contents of cellulose (43.2 wt.%) and lignin (24.7 wt.%) of RPS were higher obviously than those of CS (41.0 wt.% and 16.0 wt.%),WS (34.6 wt.% and 16.0 wt.%) and CtS (32.0 wt.% and 24.5 wt.%), and similar to those of PW (44.8 wt.% and 30.7 wt.%). The results illustrated that the chemical compositions of RPS were close to the wood but not other agricultural residues. It is well known that high lignin content is propitious to increase the mechanical strength of plant branches and trunks, and high metals (for example kalium) and silicon contents could increase the lodging-resistant of crop plants. Therefore, the high lignin content of RPS meets the requirement to mechanical strength and so decreases the needs to kalium and silicon, which could be the main reason for the low ash content.

3.2. TGA analysis

TGA and DTG curves of RPS at different heating rates are shown in Fig. 1. According to the rates of weight loss, the pyrolysis processes of RPS could be separated into three stages. The first stage was below 150 °C which was due to the water release like the most biomasses. The second stage was from 150 to 250 °C at a heating rate 10 °C/min which was owing to the degradation of hemicelluloses. The third stage was in a temperature range of 250–600 °C which was due to the pyrolysis of cellulose. However, a single weight loss peak of lignin was not found, which could be attributed to its wide pyrolysis temperature range (200–700 °C) that results in its curves overlapped by the degradation of other components such as hemicelluloses and cellulose.

As shown in Fig. 1a, with an increasing of the heating rate from 10 to 30 °C/min, the TGA curves of RPS shifted to a lower temperature, which indicated the intensity of pyrolysis reaction. It is well known that the chemical composition of biomass is very complex