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Pyrolytic behaviors of decocting residues of *Rhodiola rosea*

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ABSTRACT

Pyrolysis behaviors of decocting residues of *Rhodiola rosea* (RR) were studied by TGA and Py-GC/MS. Results indicated that with an increase of decocting time from 0 to 4 h, the contents of extractives and hemicellulose decreased from 29.15 and 5.35 wt.% to 28.18 and 3.47 wt.%, respectively, the contents of acid-insoluble lignin increased from 43.81 to 46.58 wt.%; the content change of cellulose was small. Pyrolysis processes of RR mainly occurred in seven stages and independent weight loss of lignin were found at 380–800 °C, which suggested that RR could be a perfect material to study the lignin structure. The effects of decocting time on the pyrolysis behaviors of RR were slight, mainly changing the pyrolysis progress of extractives and hemicellulose and enhancing the Activation Energy at stage3 from 96 to 110 kJ/mol. In RR pyrolysis, low pyrolysis temperature (for example 300 °C) was propitious to the formation of sugars and furans; high temperature (for example 500 °C) could be contributed to enhance the contents of linear ketones; however, moderate temperature (for example 400 °C) could be a better choice to product the linear acids and phenols. 15.44% content of 1, 6-anhydro-β-D-glucopyranose in the bio-oil at 300 °C suggested good pyrolysis selectivity of RR. Decocting treatment changed the product distributions in the bio-oil. The contents of linear ketones increased remarkably from 13.34 to 25.35% and the contents of sugars and furans decreased from 8.06 and 7.02% to 6.33 and 2.46%, respectively.

1. Introduction

Medicinal herbs have been widely used for health care in Asia, European and North America for thousands of years. Only in China, there are about 1600 medicinal herbs and over 30 million tons of herb residues were generated annually [1]. As one of the important industrial residues, the herb residues are usually landfilled and burned. Due to contain some nutrient components, these herb residues are very easy to decay, which have resulted in serious environmental problems. However, there are still not effective methods to utilize these herb residues up to now. So, the management of herb residues is changing an ongoing challenge.

Conversion of biomass to biofuel or useful chemicals has attracted lots of interests due to its renewable concept in the energy resources field. By using pyrolysis technology, biomass could be converted into bio-char, bio-oil and bio-gas. Agricultural waste, wood waste and microalgae as feedstocks have been were research to utilize better the biomass, including corn cob [2], wheat straw [3], rice straw [4], wood [5], rapeseed meal [6], algal [7] and so on. Moreover, it was also found that in the bio-oil some high value chemicals such as 4-vinyl phenol (4-VP) [8], olefin [9], 5-hydroxymethyl furfural (HMF) [10], furfural (FF) [11] and levoglucosenone (LGO) [12] and so on was included. This indicated a better application prospect of biomass. Due to the abundance in lignin, hemicellulose and cellulose, these herb residues have huge potential as feedstock of pyrolysis to product biofuel and bio-based chemicals. Some studies had been conducted to use herb residues to product bio-char [13–15] or ethanol [1].

Rhodiola rosea (RR) used as traditional medicine has a long history in Asia and European countries [16,17]. Due to including some biologically active constituents such as salidroside, butyl alcohol, sterols, glycosides, phenolic and/or cyanogenic glycosides and so on [18–20], RR has good therapeutic activity with anti-fatigue, anti-depressive and anti-allergy and have been given increasing attentions with last decades. Like most of traditional Chinese medicine, the RR was usually decocted in water, and then only the solution was used and the solid residue was discarded, which will result in environmental pollution and a waste of resources. Compared with other biomass such as corn stalk, wood residues and wheat straw, chemical compositions of RR was significantly different, which suggested special pyrolytic behaviors. After decocted, the chemical components and structures of RR were changed definitely, which implied new different pyrolysis progress. However, to our knowledge, the pyrolytic characteristics of RR included the decocting residue are not reported up to now. In this paper, the RR was decocted in a thermostatic water bath at about 100 °C for 0–4 h, respectively, and then the pyrolytic behaviors of the solid residue will be studied by thermogravimetric analyzer (TGA) and Py-GC/MS

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analysis as well as chemical component analysis. It pyrolysis kinetic parameters was calculated based to the data of TGA according to simplified pyrolysis kinetics equations.

2. Materials and methods

2.1. Materials and analysis

The RR was collected from Tibet in 2015, China. After drying in the sun, The RR was milled and stored in plastic bags. Only the fractions under 20 meshes were used for the pyrolysis experiments. RR was decocted at about 100 °Cin a thermostatic water bath for 2 h and 4 h, respectively. Then the decocted RR (DRR) and raw RR were oven-dried at 80 °C for about one day. The chemical components were analyzed according to ASTM E1758–01.

2.2. TGA analysis

A Thermo-Gravimetric (TG, Perkin Elmer STA 6000, USA) was used to perform the pyrolysis progresses from 30 to 600 °C at a heating rate of 10 °C/min. The TGA experiments were conducted under nitrogen environment (99.999%) at a flow rate of 50 ml/min.

2.3. Pyrolysis kinetic analysis

Pyrolysis kinetic parameters of RR and DRR were determined by the simplified pyrolysis kinetics equations reported in the literature [21]. The kinetic equation is described as follows:

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

Where E is the activation energy and A is the frequency factor; β is the heating rate and T is the reaction temperature; α is the fractional weight loss, which is calculated as follows:

$$\alpha = \frac{w_{\mathrm{oi}} - w_{ij}}{w_{\mathrm{oi}} - w_{\mathrm{fi}}} \tag{2}$$

Where w_{oi} is initial weight of sample, w_{ij} sample weight for the reaction i at time j, and w_{fi} is final mass of the sample in the reaction.

In most of chemical reactions, due to$\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] \approx \ln\left(\frac{AR}{\beta E}\right)$, so Eq. (1) is changed:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{3}$$

According to the slope from Eq. (3), the E is calculated; and A is also calculated according to the intercept and the E.

2.4. Py-GC/MS analysis

The fast pyrolysis was performed using a CDS Pyroprobe 5200HP pyrolyser (Chemical Data Systems) connected with a GC/MS (Perkin Elmer, Clarus 560). The RR was pyrolyzed at 300,400 and 500 °C, respectively. The DRR was pyrolyzed at 500 °C. The procedures referred the literature [22].

3. Results and discussions

3.1. Properties of feedstocks

The results of chemical components of RR were: hemicellulose 5.35 ± 0.98 wt.%, cellulose 21.69 ± 3.03 wt.%, acid-insoluble lignin 43.81 ± 1.43 wt.% and extractives 29.15 wt.% (Table 1). After decocted, its chemical components were changed. The content of hemicellulose decreased significantly from 5.35 to 3.47 wt.%. The content of lignin increased from 43.81 to 46.58%. The content change of cellulose was small. The content of extractives decreased from 29.18 to 28.18 wt.%. The dissolution of extractives and hemicellulose was the main reason for chemical components of RR during decocting.

Table 1
Chemical components of samples.

Samples	Chemical components (wt.%)[e]			
	Hemicellulose	*Cellulose*	*Lignin*[a]	*extractives*[b]
RR	5.35 ± 0.98	21.69 ± 3.03	43.81 ± 1.43	29.15
2 h[c]	4.49 ± 0.59	21.32 ± 0.51	45.16 ± 0.41	29.03
4 h[d]	3.47 ± 0.85	21.76 ± 0.27	46.58 ± 0.71	28.18

[a] Acid-insoluble lignin.
[b] obtained by difference.
[c] RR decocted for 2 h.
[d] RR decocted for 4 h.
[e] Data presented in the form of standard deviation.

The RR as a biomass was distinctive according to the chemical components. Compared with other biomass such as cotton stalks [23], corn stalks [24] and so on, the 43.81 wt.% of lignin content was higher significantly even more than that of woods [25,26]. However, the contents of cellulose 21.69 wt.% and hemicellulose 5.35 wt.% were lower than that of most of biomass. The extractives content was also higher. These suggested special pyrolytic behaviors.

3.2. TGA analysis

Fig. 1a and b showed the TG and DTG curves of RR and DRR. The pyrolysis processes of RR and DRR mainly occurred in seven stages. The first stage blow 120 °C was due to water release. The second stage from 120 to 180 °C was due to the degradation of extractives. The third stage from 180 to 250 °C was attributed to the hemicellulose pyrolysis. The fourth stage from 250 to 380 °C was the pyrolysis of cellulose. The fifth, sixth and seventh stages from 380 to 800 °C were due to the degradation of lignin. A single weight loss peak of lignin from 200 to 380 °C was not found due to overlapped by the degradation of other components like hemicellulose and cellulose.

From Fig. 1, the degradation curve of lignin was observed at a range of 380–800 °C. To our knowledge, no lignin pyrolysis curves were found in biomass pyrolysis including agricultural residues and wood residues. It is well known that only the weight loss of lignin isolated from the biomass could be found in pyrolysis [27]. To explain the weight loss at a range of 380–800 °C, milled wood lignin (MWL) from the RR was prepared according to the Beckman Method and was also used as the feedstock of pyrolysis. From Fig. 1, three weight loss stages were also observed at a range of 380- 800 °C in pyrolysis progress of the MWL, which proved that the weight loss of the fifth, sixth and seventh stages were due to the degradation of lignin in the pyrolysis of RR and DRR. This could be attributed to its especial chemical compositions, high lignin and extractives contents and low hemicellulose and cellulose contents. When the temperature was low 380 °C, the extractives, hemicellulose and cellulose almost all were degraded. It is a fact that lignin consists of benzylic hydroxyl, carbonyl groups and phenolic hydroxyl, which formed a complex structure by straight links [28]. When the temperature was low 380 °C, only aromatic rings from lignin were remained. When the temperature was over 380 °C, the aromatic rings set off the decomposition reactions/or condensation reactions [29]. So, the independent pyrolysis peaks of lignin were observed. This also suggested that RR could be a perfect feedstock used to isolate and study the lignin.

Decoction changed the pyrolysis progress of RR, especially the degradation of extractives and hemicellulose. With an increase of decocting time from 0 to 4 h, the weight loss rates decreased and the pyrolysis behavior of hemicellulose overlapped gradually with that of cellulose. During decocting, some extractives such as salidroside, butyl