Two-step pyrolysis of corncob for value-added chemicals and high quality bio-oil: Effects of pyrolysis temperature and residence time

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ABSTRACT

The effects of the first step pyrolysis temperature (T1) and residence time (RT1) on the two-step pyrolysis (TSP) were investigated by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and thermogravimetric analyzer coupled with FTIR spectrophotometer (TG-FTIR) was used to analyze the pyrolysis characteristics of corncob. T1 was classified into low temperature (T1-L: 250 °C, 300 °C and 350 °C), medium temperature (T1-M: 400 °C and 450 °C) and high temperature (T1-H: 500 °C and 550 °C). Compared with one-step pyrolysis (OSP), T1-M was the optimal condition in TSP to increase the selectivities of value-added chemicals such as acetic acid, furfural, 4-vinylphenol, 2-methoxy-4-vinylphenol and guaiacol, etc. Few acids and more hydrocarbons with content of 10.54% were acquired in the second step at T1-M, which was conducive to improving the quality of bio-oil. Different RT1 at T1-M could further increase the selectivities of specific products such as furfural at T1 of 450 °C with 10 s, toluene at T1 of 450 °C with 20 s, and acetic acid, 4-vinylphenol, 2-methoxy-4-vinylphenol and vanillin at T1 of 450 °C with 5 s, etc. Based on the results, a new polygeneration approach of TSP for efficient utilization of biomass was proposed.

1. Introduction

Biomass is an abundant renewable energy resource, which can be converted into solid, gas and liquid products [1–4]. Fast pyrolysis of biomass for bio-oil is one of the most promising technologies used for the utilization of biomass resources [5–7]. However, the adverse physicochemical properties of low calorific value, high viscosity, high acidity, poor stability and especially complicated composition restrict the utilization of bio-oil from the conventional one-step pyrolysis (OSP) [8,9]. Based on the physicochemical properties of lignocellulosic biomass, stepwise pyrolysis has been proposed to improve quality of bio-oil and concentration of value-added chemicals by releasing the products stepwise. Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses and lignin [10,11]. Hemicellulose is mainly decomposed into acids, cyclopentanones and furans products from 200 °C to 300 °C; cellulose is mainly decomposed into sugars, furans, small molecular aldehydes and ketones products from 300 °C to 400 °C; and lignin is mainly decomposed into phenols and aromatics products from 250 °C to 500 °C[12,13]. The overlapping decomposition temperature of the biomass constituents contributes to the difficulty of the stepwise pyrolysis. Therefore, it is significant to acquire the proper stepwise pyrolysis condition and explore the stepwise pyrolysis mechanism. Some literatures have reported the stepwise pyrolysis of biomass and drawn some results. De Wild et al. [12] presented that staged degasification was a conversion route to generate value-added chemicals from biomass. Hammer et al. [14] investigated the stepwise pyrolysis process with HZSM-5 catalyst for producing high quality bio-oil. Luna and Rivilli et al. [15–17] studied the stepwise pyrolysis of pine sawdust, peanut shells and olive oil industry wastes to find pyrolytic conditions appropriate to obtain chemicals from biomass in a practical way. Huang et al. [18] investigated two-stage fast pyrolysis of pine sawdust in catalytic reactor to obtained advanced bio-oil.

However, most of the related researches gave little attention to the pyrolysis mechanism and fundamental research about pyrolysis temperature and residence time, which are the most significant factors that influenced the fast pryolysis. The stepwise pyrolysis temperature and residence time can determine the pyrolysis intensity and especially the quantity of products generated in every step. In addition, the pyrolysis mechanism can be also deduced from the experiment results, which was conducive to regulating and optimizing the stepwise pyrolysis process.

Corncob is an abundant and easily available agricultural waste that often used as the material in pyrolysis experiments to obatin value-added chemicals such as furfural, acetic acid and vanillin, etc. [19,20]. In this study, thermogravimetric analyzer coupled with FTIR

spectrophotometer (TG-FTIR) was used to analyze the pyrolysis characteristics of corncob and estimate the pyrolysis temperatures. Two-step pyrolysis (TSP) of corncob was conducted in comparison with OSP by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and the effects of the first step pyrolysis temperature (T1) and residence time (RT1) on TSP were investigated. The optimum condition for high selectivity of valued-added products and high quality bio-oil was acquired. A promising scheme of stepwise pyrolysis was proposed.

2. Materials and methods

2.1. Materials

Corncob was milled and sieved to size between 0.15 mm and 0.18 mm, and then dried at 105 °C for 12 h before experiments. The ultimate analysis was conducted with an Elementary Vario EL-III cube analyzer, and the contents of C, H, N, S and O (calculated by difference) were 45.06 wt%, 5.59 wt%, 0.36 wt%, 0.19 wt% and 46.23 wt%. The proximate analysis was performed based on GB/T 28731-2012, and the contents of vapors, ash and fixed carbon were 83.31 wt%, 2.57 wt%, and 14.12 wt%. The component analysis was determined by Van Soest method, and the contents of cellulose, hemicellulose, lignin and extractives were 43.09 wt%, 35.42 wt%, 12.85 wt% and 3.85 wt%.

2.2. TG-FTIR

TG-FTIR experiment was performed by a thermogravimetric analyzer (Q500, TA Instruments, USA) coupled with FTIR spectrophotometer (Nieolet 6700, Thermo Electron, USA). In TG experiment, about 6 mg sample was heated from ambient temperature to 750 °C at heating rates of 10 °C/min, 20 °C/min and 30 °C/min, respectively. The carrier gas was nitrogen (99.999%) with a flow rate of 50 mL/min. The FTIR was connected to TGA by a gas transmission pipeline, which was heated and maintained at 220 °C. The spectrum scan frequency was 32 times per minute with a spectrum region from 500 cm^{-1} to 4000 cm^{-1} [21–27].

2.3. Py-GC/MS

Pyrolysis was performed by a CDS Pyroprobe 5250 pyrolyzer (Chemical Data Systems, USA). A filler rod, some quartz wool, 0.5 mg corncob and some quartz wool were filled to the quartz tube in succession as experimental sample. In TSP process, the heating rate of every step pyrolysis was 20 °C/ms with the carrier gas of Helium (99.999%). The pyrolysis volatiles were swept into GC/MS (Trace DSQII, Thermo Scientific, USA) and analyzed online. In TSP, the quartz tube was kept in the pyrolysis chamber after the first step pyrolysis. When the volatiles analysis of the first step was finished, the remaining sample was pyrolyzed again, and the volatiles of the second step were also analyzed by GC/MS. To observe the effects of T1 on TSP, the first step was performed at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C and 550 °C for 20 s, respectively, and the second step was all set at 700 °C for 20 s. To investigate the effects of RT1 on TSP, the first step was performed at 400 °C (10 s, 20 s, 30 s and 40 s) and 450 °C (5 s, 10 s and 20 s), and the second step was also set at 700 °C for 20 s. Compared with TSP, OSP was conducted at 700 °C for 40 s. It was necessary to point out that the fast pyrolysis temperature was lower than the set values in the brief fast pyrolysis process because of the poor thermal conductivity of biomass [28,29].

The pyrolysis volatiles were analyzed by GC/MS with a TG-5MS capillary column (30 m × 0.25 mm i.d × 0.25 μm film thickness). The inlet was set as 280 °C and the split ratio was 40:1. Helium (99.999%) was used as the carrier gas with a constant flow of 1 mL/min. The oven temperature program was from 40 °C (2 min) to 180 °C (2 min) with a heating rate of 3 °C/min, then to 280 °C (3 min) with a heating rate of 10 °C/min. The temperatures of the GC/MS interface and ion source

were held at 280 °C. The mass spectra were operated in electron ionization (EI) mode at 70 eV with *m/z* range from 45 to 650 amu. The identification of chromatographic peaks was confirmed by the NIST MS library and literatures.

The yields of volatiles cannot be determined online by Py-GC/MS due to not collecting pyrolysis products and lack of the commercially available standards for the products. Therefore, a semiquantitative analysis method was used [5,8,9,30–33]. The changes of volatile yields can be estimated by the total chromatographic peak areas. The change of each component yield can be revealed by its absolute peak area in condition of the same sample mass, because the yield was linear with its absolute peak area. The content change of a compound can be compared by its relative peak area, which did not represent accurate mass percent as response ratio needed to be considered or calibrated. The relative peak area of a product was calculated by dividing its absolute peak area by the total peak area in the same step. The experiments were repeated at least three times to ensure the reproducibility, and the standard deviation values were calculated.

3. Results and discussion

3.1. TG-FTIR analysis

3.1.1. TG analysis

The TG/DTG curves of corncob at different heating rates are shown in Fig. 1. The decomposition process went through three stages. The first stage below 200 °C had slight weight loss, which was ascribed to moisture evaporation and vitrification process. In the second stage from 200 °C to 450 °C, the weight loss was more than 72.00% with high weight loss rate, which was attributed to the severe decomposition of holocelluloses and slight decomposition of lignin [13,25,34]. There were two pyrolysis peaks in the DTG curves, and the first shoulder peak was due to the decomposition of hemicellulose. The second peak was due to the rapid decomposition of cellulose, and then the weight loss rate reduced sharply with the temperature increasing [35]. The third stage above 450 °C was the decomposition of remaining lignin and carbonization process with a slow weight loss rate [26]. The TG and DTG curves shifted to higher temperature with heating rate increasing because of the thermal hysteresis [25,36].

3.1.2. FTIR analysis

The FTIR spectrogram of volatiles released in TG process at heating rate of 20 °C/min is shown in Fig. 2. The spectra corresponding to 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C 500 °C, 550 °C and 700 °C were chosen to analyze the evolution of the volatiles, respectively. According to the change of spectral intensity with temperature increasing, the spectrogram can be also divided into three stages, which was consistent with the TG/DTG curves as shown in Fig. 1. Few volatiles were detected below 250 °C, and lots of compounds were observed in the second stage. Corresponding to the third stage of decomposition, the intensity of each compound was stable because of the slow weight loss rate. The absorption bands assignments were referenced according to the previous works [22,26,27,37–42]. The broad peaks between 3950 and 3450 cm^{-1} could be possibly ascribed to the presence of alcohol or phenolic O—H stretch. However, the intense peak in the region of 3570 cm^{-1} was due to high content of H_2O. The spectral region of 3050–2670 cm^{-1} represented C—H stretching, indicating the existence of methyl or methylene groups, which may came from CH_4. The weak peaks at around 2174 cm^{-1} and 2110 cm^{-1} was attributed to CO. The intense peak between 2400 cm^{-1} and 2260 cm^{-1} and the peak at 730–500 cm^{-1} indicated the release of CO_2 in TG process. With the temperature increasing, the intensity of the four absorption bands corresponding to the four gases respectively increased firstly and reached maximum at 350 °C, then decreased sharply and remained stable after 450 °C. A sharp peak between 1860 and 1600 cm^{-1} represented the C=O stretching vibration from organic acids, ketones