



Effects of chemical inhomogeneity on pyrolysis behaviors of corn stalk fractions



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HIGHLIGHTS

- Pyrolysis behaviors of CS fractions were different from each other.
- Only three mass loss stages were observed clearly during leaf blade degradation.
- Ear husk and stem pith were degraded more easily to produce gases at lower temperature.
- In the range of 30–230 °C, only ear husk was degraded to form CH₄.
- In the range of 30–310 °C, only CO was obtained from stem bark.

ARTICLE INFO

Article history:

Received 31 December 2013

Received in revised form 22 March 2014

Accepted 26 March 2014

Available online 13 April 2014

Keywords:

Corn stalk

Pyrolysis

TGA-FTIR

Kinetics

Activation energy

ABSTRACT

To explore the effects of chemical inhomogeneity on pyrolysis behavior of corn stalk fractions, the chemical components of stem bark, stem pith, leaf blade, ear husk and whole stalk were analyzed and their pyrolysis behaviors were studied by using the thermo-gravimetric analysis coupled with Fourier Transform Infrared Spectrometry (TGA-FTIR). Results indicated that the chemical components and pyrolysis behavior of different corn stalk fractions were significantly different from each other. The ear husk possessed the highest volatile content of 76 wt.% and the highest cellulose content of 42 wt.%, respectively. The stem pith had the highest hemicelluloses content of 25 wt.%, the least content for cellulose of 37 wt.% and lignin of 6.5 wt.%, respectively. Three stages of mass loss were observed during leaf blade pyrolysis, while four stages were observed for all the other fractions. Only the ear husk was degraded to form CH₄ in a temperature range from 120 °C to 230 °C; and only the stem bark was degraded into a form of CO in a temperature range from 230 °C to 310 °C. When the temperature was more than 310 °C, all other fractions were degraded intensively. Compared with those of other three fractions, the ear husk and stem pith had the lowest activation energy at each stage during the pyrolysis process. Chemical inhomogeneity in different corn stalk fractions was the main reason for the different behaviors.

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1. Introduction

As an alternative to fossil fuel, biomass received increasing attentions in the past decades due to the coming depletion of fossil fuels and the negative impact of their excessive usage on environment. Biomass such as agricultural wastes and wood wastes could be converted into the clean fuels including char, bio-oil and bio-gas via biochemical or thermochemical processes. Pyrolysis is preferred particular in the case of thermochemical conversion of

biomass, which could produce char and volatile organic materials. These products can be used to produce chemicals, heat, fuels, and electricity [1].

The pyrolysis of agricultural waste had been well documented. The pyrolysis behaviors of corncobs [2], grape residues [3], rice straws [4], cherry seeds [5], rapeseed meals [6], algal [7], tobacco residues [8], etc. had been studied for different purposes. The studies of biomass pyrolysis had indicated that chemical components of biomass not only have very important effects on their pyrolysis behaviors [9–12,13], but also determine the outputs and the properties of pyrolytic products. For example, corncob is widely used to produce furfural due to its richest content of pentosan. Corn stalk (CS) is always used as a pyrolysis feedstock due to its largest yields.

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For example, about 200 million tons CS are produced in China each year [14]. The CS fractions, including the ear husk, leaf blade, stem bark and stem pith, possess different chemical components, which may result in considerable impacts on the efficiency of bioconversion [15,16] and chemical conversion [17] of CS. Worasuwannarak et al. [4] demonstrated that the chemical inhomogeneity of rice straw fractions is a major reason for different pyrolysis behavior of rice straw. However, little information is available on the effects of chemical inhomogeneity on pyrolysis behaviors of corn stalk fractions.

Technique of thermogravimetric analysis coupled with Fourier Transform Infrared Spectrometry (TGA-FTIR) is an effective tool in investigating the correlation between chemical structure and degradation mechanism, providing a quantitative method to determine the kinetic parameters in thermal degradation reactions. TGA-FTIR method has been widely used in polymer [18–21] and biomass pyrolysis studies [10,22–24]. To study the effects of chemical inhomogeneity on pyrolysis behaviors of corn stalk fractions, we examined the ear and stem pith, whole stalk, leaf blade only had pyrolysis progress of CS fraction by using the TGA-FTIR technique.

2. Materials and methods

2.1. Materials and analysis

CS was harvested and collected from a local farm in Beijing suburb in 2011 and stored in plastic bags. The moisture content ranges from 8 to 10 wt.%. The CS samples were manually separated into whole stalk, ear husk, leaf blade, stem bark and stem pith. Each fraction was milled and the fractions under 20 meshes were used for the pyrolysis experiments. The whole stalk was aboveground components of corn plant, comprised of leaves 24 wt.%, stalks (including stem bark, stem pith and node) 46 wt.%, ear husk 25 wt.% and others 5.0 wt.%. The chemical components and proximate analysis of CS fractions were analyzed according to ASTM E1758-01 and GB/T 28731-2012, respectively.

2.2. Experimental methods

The pyrolysis progress of CS fractions was conducted in a Thermo-Gravimetric Analyzer (TGA, Perkin Elmer STA 6000, USA) coupled with Fourier Transform Infrared Spectrometer (FT-IR, Perkin Elmer Spectrum100, America) from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen environment (99.999%) at a flow rate of 50 mL/min. The FT-IR spectrum scope was in the range of 4000–500 cm⁻¹.

2.3. Pyrolysis kinetic analysis

Pyrolysis kinetic parameters were determined by the simplified pyrolysis kinetic equation [25]. The kinetic equation is described as follows:

$$\frac{dx}{dt} = kf(x) \quad (1)$$

where $k = Ae^{-E/RT}$ is the apparent reaction rate constant according to the Arrhenius equation; $f(x)$ is the pyrolysis reaction function. In this case, the $f(x)$ is approximated as $(1-x)^n$, where n is the apparent reaction order and x is the fractional weight loss (g), which is calculated as follows:

$$x = \frac{w_{oi} - w_{ij}}{w_{oi} - w_{fi}} \quad (2)$$

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

By combining with Eq. (2), the logarithmic form for Eq. (1) is given by:

$$\ln \left(-\frac{dw_{ij}}{w_0 dt} \right) = \ln k + n \ln \frac{w_{ij}}{w_0} \quad (3)$$

The k and n can be calculated by using fitted line from Eq. (3). The n is the slope of the fitted line and the $\ln k$ is its intercept at the origin.

To obtain the activation energy E and the frequency factor A (s⁻¹), the logarithmic form of k is used:

$$\ln k = \ln A - \frac{E}{RT} \quad (4)$$

According to the k value at different temperature, a fitted line is obtained from Eq. (4), and the E is calculated from its slope (kJ mol⁻¹ K⁻¹).

3. Results and discussion

3.1. Properties of raw materials

The results of proximate analysis and chemical components of samples are listed in Table 1. The highest ash content was 9.6 wt.% in whole stalk, whereas the lowest level was 2.8 wt.% in ear husk. The ash contents in leaf blade, stem bark and stem pith were 8.8, 3.2 and 3.6 wt.%, respectively. Ear husk has the highest volatile content of 76 wt.%. Leaf blade and whole stalk had similar volatile content of 70 and 69 wt.%, respectively. The differences of fixed carbon content in the five samples were small.

The main chemical components differed in the tested samples. Stem pith had the highest hemicelluloses content of 25 wt.%, while leaf blade had the lowest content of 19 wt.%. Ear husk, stem bark, and whole stalk had similar hemicelluloses contents, ranging from 21 to 23 wt.%. The lowest cellulose content of 37 wt.% was detected from stem pith. Stem bark, ear husk, leaf blade and whole stalk had 41, 42, 40, and 41 wt.% cellulose contents, respectively. The acid-insoluble lignin content differed significantly among five samples ranging from 6.5 to 18 wt.%. The 6.5 wt.% of acid-insoluble lignin content was from stem pith, and the 18 wt.% was from stem bark.

3.2. Pyrolysis analysis

The TGA and DTG curves of the five fractions are shown in Fig. 1. The pyrolysis processes of whole CS, stem pith, stem bark and ear husk all occurred in four stages, whereas the occurrence of pyrolysis of leaf blade was in three stages. The first stage weight loss in a range of 2.17–5.04 wt.% at 120 °C or lower was due to water release for the five samples. The second stage weight loss in a range of 0.0–6.7 wt.% between 120 °C and 230 °C was attributed to the degradation of extractive compounds with poor thermal stability, such as amino acids, fructopyranose and protein [26]. Comparison of DTG curves indicated that the five fractions have different pyrolysis behaviors in the second stage. In the second stage, the pyrolysis process was not observed for the leaf blade, suggesting that the leaf blade had lower extractive compound content. The differences of weight loss rates among stem bark, whole stalk, stem pith and ear husk could be contributed to the different chemical contents and types of extractive compounds.

The third stage weight loss in a range of 18–24 wt.% between 230 and 310 °C was due to the pyrolysis of hemicelluloses, a result that is consistent with the literature [27]. The pyrolysis of cellulose occurred in the fourth stage between 310 and 600 °C. Unlike the pyrolysis of hemicelluloses, cellulose showed a faster pyrolysis

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