



Conversion and extracting bio-oils from rod-shaped cornstalk by sub-critical water



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ABSTRACT

The rod-shaped cornstalk sample was selected to investigate the generation of bio-oils (including water-soluble oil and heavy oil) by sub-critical water under different reaction temperatures (240–350 °C) and extraction times (0–120 min). The gas, the water-soluble oil extracted by *n*-hexane and heavy oil extracted by acetone from the residue were collected and disposed, respectively. The gas chromatography-mass spectrometer (GC-MS) analysis of water-soluble oil showed that phenols were the major compounds. The pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis of heavy oil showed that it was primarily consisted of phenols, carboxylic acids, aromatic ketones, and nitrogen- and sulfur-containing compounds. The results demonstrated that the optimum liquefaction condition in sub-critical water was at 260 °C and 15 min, and the highest bio-oil yield could be reached 33.00%. The results of experiment indicated that the structure of the lingocellulose (lignin, cellulose and hemicellulose) in the rod-shaped cornstalk was able to be broken down by sub-critical water at relatively low temperature and short extraction time without any catalyst and organic reagent.

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1. Introduction

As we all know, cornstalk as the byproducts of corn crop are a lot of waste. The methods of combustion and burial are usually utilized to eliminate cornstalk, which caused a lot of pollution. But cornstalk contained rich lignocelluloses [1–3], so it has great potential utilization as energy resource. The cornstalk is mainly consisted of cellulose, hemicellulose and lignin, and each of the components can be set as the raw material of valuable chemicals [4–8]. The utilization of lingocellulose will offer important economic and environmental benefits due to its renewable property [9–11]. So, many efforts, including direct combustion [12], thermo-chemical liquefaction [13,14], bio-chemical process [15] and agro-chemical process [8], have been tried to convert cornstalk to fuels and chemicals.

Generally, the temperature between 100 °C and 374.2 °C was defined as sub-critical water. As a new reaction medium, sub-critical water with higher density and larger ionization constant [16–19] has excellent solubility for organic matter and acid-base

catalytic function [16,20] for the decomposition of organic matter. So it exhibited different advantages comparing with traditional biomass gasification [21–23]. In addition, the reaction temperature and pressure of sub-critical water are lower than that of supercritical water. So it has lower requirements for reactor materials in terms of corrosion and compression performance. It can shorten extraction time and improve the quality of the extracts. Zhu et al. [24] obtained amino acids production from fish proteins hydrolysis in sub-critical water. Asghari and Yoshida [25] obtained 5-hydromethylfurfural from fructose in sub-critical water. Overall, the sub-critical water is an excellent medium for fast and efficient reactions [19,20,26,27].

Currently, extensive attempts to develop the biomass resource in order to obtain more valuable production have promoted the development of hydrothermal technologies. With the appearance of bio-oil [28], it is meaningful for relieving the pressure on high quality fuel supply. Therefore, many researchers have studied the hydrothermal liquefaction of various kinds of biomass to obtain bio-oils. Karagöz et al. [29] separated and collected the oil from the sawdust, rice husk, lignin and cellulose by hydrothermal treatment at 280 °C for 15 min. Demirbas [30] obtained the oil from beech wood and its yield reached 28.00% at 376 °C for 25 min. Qian et al. [31] obtained bio-oils from woody biomass by sub-critical water at 380 °C with sodium carbonate as the catalyst. Shi et al. [32] con-

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verted cornstalk to bio-oils in sub-critical water and investigated ultrasonic pretreatment on the yield and chemical composition of bio-oils. Song et al. [33] converted cornstalk to bio-oils in sub-critical water and investigated the effect of catalyst on the yield of bio-oils. Liu et al. [34] applied sub-critical water in the hydrothermal liquefaction cornstalk and gained the bio-oils. Although the sub-critical water has been applied in the extraction of biomass, the studies used powder sample (0.015–0.250 mm) as raw material, which need to be crushed thoroughly. The research of rod-shaped cornstalk thermal decomposition by sub-critical water is rarely reported. Moreover, there is lack of comprehensive and detailed analysis of liquefaction products in the previous literatures.

This paper not only explores the yields of liquefaction products extracted from the rod-shaped cornstalk by sub-critical water, but also analyzes the compositions of liquefaction products and organic gases formed during the liquefaction process. The objective is to gain bio-oils from rod-shaped cornstalk at relatively low temperature and short extraction time without any catalyst and organic reagents. We hope it could make a reference in the industrialization utilization of rod-shaped cornstalk.

2. Materials and methods

2.1. Materials

The fresh sample of cornstalk used in experiments was taken from Changchun City, Jilin Province, China. The raw cornstalk was cleaned using deionized water and cut into 3–5 cm long and 1 cm thick as rod-shaped sample. After drying in an oven at 105 °C for 4 h, part of the rod-shaped sample was crushed by a pulverizer (FW100, Tian Jin Taisite Instruments Co., Ltd., China) and sieved by a 100 mesh screen (less than 0.015 mm in diameter) as powder sample. The chemical composition of the raw cornstalk sample had been determined according to the reported methods [35]. The components of the raw cornstalk were consisted by 46.20% cellulose, 37.50% hemicellulose, 15.30% lignin. The cornstalk sample was buried by a muffle furnace (SX2–4–10, Energy Conservation Enterprise in Shenyang, China) at 600 °C for 2 h for obtaining the ash in the raw material (0.80% ash on a dry basis). The water purified by ultrapure water system was used in all of the experiments. Acetone and *n*-hexane used for extracting bio-oils were purchased from Sinopharm Chemical Reagent Co., Ltd., China, which were of suitable analytical grade and used without further purification.

2.2. Experimental

2.2.1. Preparation of liquefaction products

The hydrothermal experiments were performed in a 1 L stainless steel autoclave that was designed to achieve high temperature and pressure by Tongda Reflection axe Industry factory of Dalian, China. Adding different amounts of cornstalk samples and 500 mL water into the reactor in each experiment. Then, the autoclave was heated to 240, 260, 280, 300, 320, and 350 °C rapidly with a heating rate of 10 °C/min controlled by an electric controller. And the inside temperature of reactor was supervised through a temperature probe in the reactor that connected to the electric controller. Under these conditions, the pressure, which were almost provided by vapor pressure of water at different experiment temperatures, were about 3.2, 4.1, 6.1, 8.2, 11.4, and 16.0 MPa, respectively. The experiment at each experimental temperature was held for 0, 15, 30, 45, 60, and 120 min, respectively. After liquefaction, the electric controller was turned down and then the high temperature autoclave was allowed to cool down to room temperature within 4 h. The schematic diagram for sub-critical water extraction is shown in Fig. 1. Every experiment was repeated three times and the stan-

dard deviation which was determined from three experiments was found to be less than 1.0%. The experimental data taken from the mean value of three time experiments ensured the reliability of the conclusions.

2.2.2. Collection of gas phase

After the hydrothermal liquefaction, the reaction system was divided into the gas phase lump, the water-soluble lump and the water-insoluble lump, respectively. The gas phase was collected by connecting gas sampling bag with the needle valve on the autoclave. The sampling bag was weighted by the electronic balance before and after the collection of gas, respectively. So the gas mass was obtained.

2.2.3. Extraction of water-soluble oil

100 mL of liquefaction products was and 30 mL of *n*-hexane were added to a separatory funnel for extracting water-soluble oil. It was shocked for 5 min and stood for 10 min. After the water (lower solution) was put off, the extraction fraction (upper solution) was obtained and 2 g of Na₂SO₄ was used to remove the water in water-soluble oil. After that, the water soluble oil was condensed to 2 mL by the rotary evaporator at 60 °C and the concentrated solution was filtered by microfiltration membrane for the detection of GC–MS.

Additionally, 100 mL of liquefaction products was transferred into the flask and it was separated by the method of vacuum distillation at 60 °C in a water bath. The water-soluble oil was obtained in the flask and weighted by the electronic balance for obtaining the water-soluble oil mass.

2.2.4. Extraction of heavy oil

The water-insoluble lump was consisted of two parts: the heavy oil and solid residue. The heavy oil was extracted repeatedly for 24 h by acetone. The acetone was removed by a rotary evaporator at 45 °C to obtain heavy oil which was analysed by Py–GC–MS. The remaining solid residue was dried in an oven at 105 °C for 12 h. The heavy oil mass was obtained by weighting the flask before and after the rotary evaporation experiments with the electronic balance. The solid residue was weighted by the electronic balance. The water-soluble oil and the heavy oil were collectively called bio-oil.

2.3. Analysis methods

2.3.1. GC–MS analysis

An Agilent 7890A gas chromatograph equipped with an Agilent 5975N mass spectrometer (GC–MS) was employed to detect the compounds in the water-soluble oils. Gas chromatography was performed using a HP-5MS column (30 m × 0.25 mm ID × 0.25 μm film thickness). Helium was used as the carrier gas. The inlet temperature of GC–MS was set as 260 °C and split ratio was 1:20. The oven temperature was maintained at 60 °C for 3 min, followed by a heating rate of 5 °C/min to 280 °C and held 40 min. The MS detector was operated as follows: scan mode range from 40 to 400 *m/z*, ion source temperature at 280 °C and ionization energy at 70 eV.

The collected gas samples were detected by GC with a flame ionization detector (GC–FID) and the compounds in gas samples were identified by GC–MS. The capillary column CP-PoraBOND Q 25 × 0.25 with the porous divinyl benzene homopolymer was used as the stationary phase. The inlet temperature was held at 40 °C and the split ratio was 1:20 with N₂, H₂ and compressed air as the carrier gases. The GC–MS operating parameters were set as follows: the temperature program was held at 40 °C for 2 min and then heated from 40 to 150 °C at 20 °C/min and held 15 min. The MS detector was operated with the scan mode ranged from 40 to 400 *m/z* at 230 °C and ionization energy at 70 eV.

The data were collected by the Agilent MSD ChemStation software. The unknown compounds in water-soluble oil and gas

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