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Hemicellulose in corn straw: Extracted from alkali solution and produced 5-hydroxymethyl furfural in HCOOH/HCOONa buffer solution[☆]

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ABSTRACT

Hemicellulose in corn straw is a group of complex heteropolysaccharides which are composed of different sugar units, including mannans, xylans, arabinans and galactans. This study developed a simple and practical process for production of 5-hydroxymethyl furfural (HMF) using hemicellulose that was extracted from corn straw. In the hemicellulose degradation process HCOOH/HCOONa was used as buffer solution, and the optimum conditions for maximum HMF yield were explored. Various extraction conditions including NaOH concentration, reaction time, temperature, solid-to-liquid ratio and precipitant were tested for hemicellulose obtaining, giving the optimum condition of 55 °C, 4 h, solid-to-liquid ratio of 1:10, 1.5 mol·L⁻¹ NaOH solution and ethanol as precipitant with the yield of 34.16%. Dehydration of hemicellulose under HCOOH/HCOONa buffer solution process, using solution medium of pH = 0.8 hydrolyzed hemicellulose in corn straw at 190 °C after 190 min and 82% of HMF yield was achieved.

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1. Introduction

Lignocellulosic biomass is a renewable and abundant resource which has great potential to be converted to chemical feedstocks in the future. The main components in the lignocellulosic biomass are cellulose (30%–50%), hemicellulose (20%–40%) and lignin (10%–24%), depending on species [1]. The three essential components in the biomass are of extensive applications. Cellulose could be used as feedstock for oxygenated materials or even be reduced to give petroleum-like starting materials. Lignin could be used as a source for aromatic compounds if it can be depolymerised in a controlled fashion. In addition, hemicellulose in corn straw is an amorphous heteropolysaccharide consisting of hexose or pentose units, such as mannans, xylans, arabinans and galactans [2]. Due to the compositional complexity of hemicellulose, the hydrolysis reaction is constituted of parallel paths that lead to a complex mixture of sugars (xylose, glucose, arabinose, and mannose) and organic acids, such as formic acid, acetic acid and levulinic acid [3]. One possible structure for the hemicellulose [4] in corn straw was illustrated in Fig. 1.

However, due to the complexity of hemicellulose structure, limited research has been reported on the degradation of hemicellulose. In tradition, considerable efforts had been devoted to the conversion of cellulose or a few hexoses into HMF, which emerged as promising options to replace fossil fuel-based organics for the production of

valuable biofuels and chemicals [5], such as *N,N*-dimethylformamide [6], 5-ethoxymethylfurfural [7], and levulinic acid [8]. Antal and Mok used H₂SO₄ as a catalyst to degrade fructose in subcritical water at 250 °C, and achieved HMF yield of 53% [9]. Jiang *et al.* found that more than 69.2% yield of HMF could be achieved at 170 °C for 70 min in the dehydration of sugars in the aqueous/butanol media, which was enhanced by using formic acid [10]. Pandey *et al.* carried out a continuous dehydration of D-glucose into HMF under mild conditions, using SO₃H-functionalized acidic ionic liquids as catalysts and H₂O-4-methyl-2-pentanone biphasic system as solvent [11]. Herein reported a new reaction pathway in polar aprotic solvents (*i.e.* THF) without the presence of water to produce HMF from cellulose under mild reaction conditions (140–190 °C and 5% H₂SO₄) and gained the highest HMF yield of 44% [12]. Furthermore, Jae-An Chun revealed that using HCl–CrCl₃ as co-catalysts could efficiently promote the conversion of starch to HMF and the yield was as high as 73% [13].

Lignocellulosic biomass has a very strong resistance to microbial and enzymatic deconstruction due to many factors such as the crystallinity of cellulose, cell wall polymer chemistry and particle size [14]. Therefore, pretreating these biomass materials or separating and extracting more pure components by chemical processes might lead to easy ways for subsequent degradation. After the pretreatment, the hemicellulose derived from the biomass such as corn straw would lead to a high potential application. Hence, in this work, hemicellulose which was extracted from corn straw was chosen as our main raw material. Then it was converted into HMF in the acidic buffer solution of formic acid/sodium formate buffer system. The buffer solution of formic acid and

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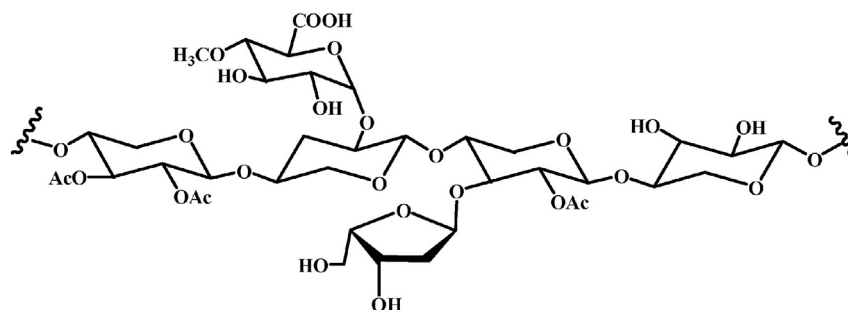


Fig. 1. The structure of hemicellulose.

sodium formate not only provides a suitable reaction media but also act as an effective catalyst with the advantages as follows:

- ① Using the acid buffer solution with precise pH value could improve the catalytic selectivity of hemicellulose to the preparation of HMF;
- ② Choosing the buffer solution might avoid excessive using of organic acids so as to reduce the corrosion on equipments;
- ③ This method turned out to be an affordable way to save economy cost, and the development of process conditions was thought to be practical in applications.

Since the buffer system has advantages to maintain a constant and specific pH than other solutions, the degradation process is expected to be stable. The aim of the study was to investigate the degradation of hemicellulose in a buffer solution and to explore the optimal condition including reaction temperature, time and pH to achieve the maximum yield of HMF.

2. Experimental

2.1. Materials

Corn straw used in this study was obtained from the experimental farm of Hebei Academy of Agriculture and Forestry, China. It was oven dried at 60 °C for 24 h after deionized water was washed. Then it was ball-milled and screened after it was chopped into small pieces to achieve a size of less than 0.25 mm and larger than 0.18 mm prior to the hydrolysis. Methyl alcohol (HPLC Grade) and acetonitrile (HPLC Grade) were supplied by Concord Technology Co. Ltd., China. The rest of the chemicals used in the experiments were of analytical grades and purchased from Tianjin Kermel Chemical Reagents Co. Ltd., China. Ultrapure water was prepared in a lab by Ultrapure Water Polishing System.

2.2. Optimization the extraction of cellulose, hemicellulose in corn straw

The corn straw powder pretreated above was soaked in 1.5 mol·L⁻¹ aqueous NaOH solution with a 1:10 powder to extractant ratio (g·mL⁻¹). The dispersions were allowed to stir gently for 4 h at 55 °C in a glass beaker and then filtered to get the filtrate. The residue was filtered off and washed thoroughly with water until the filtrate was neutral, and then dried in the oven at 50 °C for 16 h. The filter liquor was neutralized to pH = 6–7 with 10 vol% HCl, and the solubilized hemicelluloses were isolated by precipitation of the concentrated filtrates with four volumes of 95 vol% ethanol. After filtration, the isolated hemicellulose was thoroughly washed with 70 vol% ethanol and dried in vacuum for 24 h. The alkali lignin was obtained by precipitation at pH = 1–2 adjusted with 10 vol% HCl from the corresponding supernatants after evaporation of ethanol. The isolated lignin preparations were purified by washing with acidified water (pH = 2.0), and then freeze-dried. The ashes in corn straw were calcinated in the muffle furnace (Shenyang, RJM-28-10, China) at 500 °C for 200 min. All the contents of cellulose lignin and hemicellulose represented the mean of at least triplicate.

In this process, different conditions including temperature, extraction time, solid-to-liquid ratio, precipitants, and the concentration of

NaOH solution were changed to achieve the maximum of hemicellulose.

2.3. Molecular weight distribution and FT-IR characterization of hemicellulose

The molecular weight of soluble hemicellulose was determined by gel permeation chromatography (GPC) of the high performance liquid chromatography system (HPLC) (Shimadzu LC-20AD, Japan) equipped with a Ultrahydrogel™ 250 (7.8 mm × 300 mm, Waters) column. The temperature of column compartment was set to 65 °C, the mobile phase was ultrapure water at a flow rate of 0.8 mL·min⁻¹, and injecting sample solution of 20 μ L in volume was run for 15 min. The recommended maximum pressure for this column was 20 MPa, and all the experiments were conducted in accordance with this upper limit. All the molecular weight distribution and related polymer-relevant parameters were calculated by Shimadzu Chemstation GPC add-on software.

The spectra of hemicellulose before and after degradation were characterized by Fourier transform infrared spectroscopy (FT-IR) (Bruker, Vector 22, Germany). The progress was carried out by a diffuse reflectance accessory with KBr as standard. For sample preparation about 100 mg of KBr and with 1 mg of sample were ground in an agate mortar. The sample mixture was scanned in the middle infrared range from 4000 cm⁻¹ to 500 cm⁻¹ at a spectral resolution of 4 cm⁻¹.

2.4. Degradation of hemicellulose under formic acid/sodium formate buffer solution and product analysis

The catalytic hydrolysis of hemicellulose was performed in a heavy iron batch autoclave equipped with a liner of polytetrafluoroethylene. As a typical run, 0.3 g hemicellulose powder and 30.0 mL formic acid/sodium formate buffer solution of different pH were charged in the reactor, tightened the cover of autoclave and the mixture was then heated from 150 °C to 230 °C (interval of 20) with duration of 150–230 min (interval of 20) and the pH 0.6 to 1.0 (interval of 0.1) in the oven.

Monosaccharide analysis was performed on the HPLC of Shimadzu Prominence System equipped with two LC-20AD quaternary gradient pumps, an evaporative light scattering detector (ELSD) (Alltech, LC-2000ES, USA). Pure air was used as the ELSD nebulizer gas (2.0 L·min⁻¹), drift tube temperature was set to 95 °C. Separation was primarily achieved on an XBridge BEH Amide Column (4.6 mm × 250 mm, 3.5 μ m, Waters) and the column oven maintained at 30 °C. The solvent gradient consisted of a linear increase in the amount of water in acetonitrile (H₂O, vol%): 0–1 min (10%), 1–70 min (10%–50%). The flow rate was set to 1.0 mL·min⁻¹, and injections of 5 μ L were adopted.

The identification of product was conducted on the NMR Spectrometer (Bruker AV-400, Germany). The degradation liquid was repeatedly extracted with ethyl acetate three times, and then the extract solution was distilled and concentrated under reduced pressure at 28 °C. The concentrated solution was purified through column chromatography with GF254 silica gel (eluant: the ratio of ethyl acetate to dichloromethane was 1:10). The purified product was identified by NMR, the main product of hemicellulose degradation was HMF, and its NMR data was as follows:

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