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Xylo-sugars production by microwave-induced hydrothermal treatment of corncob: Trace sodium hydroxide addition for suppression of side effects

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ABSTRACT

To overcome the recalcitrance of lignocellulose structures that hinders the robust bioconversion of biomass for bioethanol and lignin-coproduct productions, efficient approaches are needed to remove hemicelluloses. In this study, a microwave-induced hydrothermal pretreatment of corncob was developed to improve xylo-sugars (xylose, xylooligosaccharides and xylan) yields and to reduce the hemicelluloses loss by controlling NaOH and the severity factor. During this process, the severity factor ranged from 2.30 to 4.30 and the low concentration of NaOH below 0.32% were considered. The results showed that NaOH had a significant impact on xylo-sugars yields as well as the severity factor. The highest xylo-sugars yield of 88.71% was achieved when 0.005% NaOH was employed as the deacetylation agent and the severity factor was 4.00. Meanwhile, the unknown loss of hemicelluloses was limited to 1.51% (based on the total hemicelluloses in corncob) and the formation of furfural was also limited at the low level (1.72%).
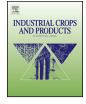
1. Introduction

Fossil oil has been, until now, the main resource to manufacture fuels, energy products and chemicals, while the massive use of fossil resource simultaneously causes major environmental problems (Cox et al., 2000; Xin et al., 2015). Thus more and more attentions have been focused on the exploitation of the renewable resource due to fewer environmental problems generated by biorefinery than fossil refinery. Lignocellulose is considered as the promising alternative resource (Ragauskas et al., 2006) because of its rich source, low price, environmental friendliness and renewability. However, owing to their physic-chemical structures and complicated components, lignocellulose presents a robust recalcitrance to decomposition or hydrolysis (Lee et al., 2015; Mazzotta et al., 2014). Therefore, it is of importance to break down the structure barriers by the pretreatment for lignocellulosic biomass conversion to high valued chemicals and liquid biofuels (Balat et al., 2008).

In contrast to the stubborn crystalline structure of cellulose, hemicelluloses are made up of amorphous heteropolysaccharides containing pentose and hexose units (Ebringerová et al., 2005). And they link with lignin to form lignin-carbohydrate complex which makes cellulose inaccessible during the process of hydrolysis (Mamman et al., 2008). Thus, the pretreatment of lignocellulose is conducted to increase the accessible surface area of cellulose for further reaction by dissolving hemicelluloses and/or lignin and/or altering lignin (Hendriks and Zeeman, 2009). But if hemicelluloses and lignin dissolved cannot be efficiently converted into high added products, it does not be conducive to the economical-functionality conversion of lignocellulosic biomass (Li et al., 2013). Additionally, furaldehydes (furfural and 5-hydroxymethylfurfural) and phenolic compounds might be generated due to the excessive degradation of hemicelluloses and lignin, which are undesired and harmful for the subsequent process of the hydrolysate conversion (Jönsson et al., 2013). Hence, the ideal pretreatment will be employed to obtain high cellulose recovery, high hemicelluloses dissolution rate for

production of high value-added products, and low concentration of byproducts.

Depending on the processes and conditions used, pretreatments of lignocellulose are divided into acid hydrolysis, hydrothermal pretreatment, wet oxidation, delignification pretreatment, alkaline pretreatment and so on (Carvalheiro et al., 2008). Among them, the hydrothermal pretreatment is known as an environmentally friendly technology owing to several advantages: water is used as the action medium (Garrote et al., 2001); hemicelluloses can be converted into soluble saccharides with high yield and less byproducts (Allen et al., 1996; Saska and Ozer, 1995); corrosion of equipment is limited and environmental impact is reduced (Saska and Ozer, 1995). As a consequence, the hydrothermal pretreatment is a promising technique to disrupt the lignin-hemicellulose-cellulose complex for enhancing cellulose hydrolysis and improving sugar release performance. In this process, hemicelluloses such as L-arabino-(4-O-methylglucurono)-D-xylan can be degraded into xylo-sugars (xylose, xylooligosaccharides and xylan in hydrolysate), arabinose, acetic acid and furfural, while the yield and pre-hydrolyzed components mainly are determined by the pH and severity factor (SF) of pretreatment. Xylo-sugars as the high value-added products can be commercially used as food additives, nutraceuticals, cosmetics, pharmaceuticals or agricultural products (Xiao et al., 2013).

During the hydrothermal pretreatment, hydronium ions, stemming from the auto-ionization of water, lead to the hydrolysis of glycosidic linkages and acetyl groups in hemicelluloses at the first stage. Subsequently, acetic acids produced by deacetylation cause a decrease in the pH of hydrolysate and then act as the catalyst to sustain the reaction with a higher rate (Carvalheiro et al., 2008). Therefore, deacetylation plays a dramatic role in the hydrothermal reaction. Selig and co-authors clarified that the removal of acetyl groups from corn stover improved the hemicelluloses hydrolysis ratio since the presence of acetyl groups has an essential effect on the ability of the chemicals to access and hydrolyze xylan (Selig et al., 2009). Jiang and Xu reported a stepwise pretreatment on corn stalk by alkali deacetylation combined with liquid hot water to enhance enzymatic hydrolysis. The result showed that the combined pretreatment increased glucose yield due to the more acetic acid produced, also enhanced energy utilization efficiency (Jiang and Xu, 2016).

In this study, a feasible pretreatment of corncob was implemented to efficiently restrain side reactions (xylo-sugars degradation) and reduce the loss of hemicelluloses during the microwave-induced hydrothermal pretreatment (MIHP) by controlling the NaOH concentration and SF. Hemicelluloses in corncob were expected to convert into xylo-sugars as much as possible while the side effects, such as the formation of furfural, were inhibited during MIHP. The xylo-sugars yields, components recoveries and hemicelluloses mass balances after pretreatment were comparatively investigated at varying sodium hydroxide concentrations (0-0.005%) and SF (2.30-4.30), respectively. The behaviors of inhibitors (furaldehydes and phenolic compounds) in different reaction conditions were also investigated by gas chromatography-mass spectrometry (GC–MS). Moreover, the chemical compositions of solid residue as well as the surface morphology and crystallinity were detected.

2. Materials and methods

2.1. Raw material

Corncob used in this study was collected from a farm in Shandong province, China. The dried corncob was ground into particles with a size of 60–80 mesh and extracted by soxhlet extractor with acetone/ethanol (2:1, v/v) for 8 h. The extractive-free power was oven dried to constant weight afterwards. Sodium hydroxide (96.0%, AR) was supplied by Guangdong Chemical Reagent Engineering-technological Research and Development center. Sulfuric acid (98%, AR) and CH_3CN ($\geq$99.9%, HPLC) were purchased from Tianjin Kermel Co., Ltd. (Tianjin, China). The standard reagents (D-xylose, D-glucose, L-arabinose, furfural, etc.) were provided by Sigma-Aldrich. The main components of dewaxed corncob were (w/w): glucose 37.76%, xylose 32.59%, total lignin 15.05%, arabinose 4.57%, galactose 1.91%, and ash 1.18%. All reagents were used without any purification.

2.2. Hydrothermal pretreatment

In order to investigate the influence of the NaOH concentration and SF on MIHP, experiments were carried out as a function of these two variables.

2.2.1. NaOH concentration variable

MIHP was performed in a 100 mL closed-vessel PTEF (polytetrafluoroethylene) microwave reactor (600 W, GAS-800, Beijing Xianghu Science and Technology Development Reagent Co., Ltd., Beijing, China). Prior to the reaction, dewaxed corncob and a certain amount of NaOH was dispersed into ultrapure water at a solid-liquid ratio of 1:20 ($g\,mL^{-1}$) with the help of ultrasonic cleaner (15 min, room temperature, 40 KHz), and then all pretreatments were conducted at 160 °C for 60 min (SF of 3.54). After MIHP, the liquid and solid fractions were separated by vacuum filtration. The solid residue was washed with ultrapure water several times and dried for the characteristic analysis.

2.2.2. Severity factor variable

The SF, a single parameter containing integrative effects of both time and temperature, was employed to give a simplified, empirical interpretation of the measured effects (Abatzoglou et al., 1992; Vegas et al., 2008). SF can be calculated as follow:

$$SF = \log(t \times e^{(T_H - T_R)/14.75}) \tag{1}$$

where t is reaction time (minute), T_H is the pretreatment temperature (°C), and T_R is a reference temperature (often 100 °C).

According to the results of experiments used NaOH concentration as variable, the most optimal concentration of NaOH was determined. The ultrasound-treated mixture at the solid-liquid ratio of 1:20 ($g\,mL^{-1}$) was transformed to the high-pressure microwave reactor and then reacted under different SFs (2.30–4.30) when NaOH concentration was optimal or zero. The reacted suspension was also separated by filtration for the characteristic analysis.

2.3. Analysis of the hydrolysate

The pH value of liquid after reaction was measured by acidometer (PHSJ-3F, Shanghai INESA Scientific Instrument Co., Ltd). Monosaccharides (glucose, xylose and arabinose) and acetic acid were analyzed by a high-performance liquid chromatography (HPLC) using Aminex HPX- 87H (BIO-RAD) column. The mobile phase was 5-mM H_2SO_4 at a flow rate of 0.5 mL min^{-1} and the temperature of the column was 50 °C. Furfural and HMF were quantitatively determined by the HPLC with a C18 column. A solution of ultrapure water to acetonitrile (85/15, v/v) was employed as a mobile phase with a 1.0 mL min^{-1} flow rate at 30 °C. Concentrations of XOS (from xylobiose to xylohexaose) were measured by HPX-42A (BIO-RAD) column and mobile phase was distilled water with a 0.3 mL min^{-1} flow rate at 70 °C. Xylan in the pretreatment hydrolysate was back-calculated after post-hydrolysis into