



Evaluating and optimizing pretreatment technique for catalytic hydrogenolysis conversion of corn stalk into polyol



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HIGHLIGHTS

- Steam explosion coupled with alkali was a better method for corn stalk treatment.
- This method removed 84.16% of hemicellulose and 71.83% of lignin in corn stalk.
- This method had no significant effect on the glucose loss.
- The activity of catalytic hydrogenation in Ni–W₂C/CSAC was mainly come from W₂C.
- About 72.74% of polyol was converted from pretreated corn stalk using Ni–W₂C/CSAC.

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ABSTRACT

A combinative pretreatment technology of steam explosion (SE) and alkali was applied to enhance hydrogenolysis conversion of corn stalk into polyol with Ni–W₂C or Fe–Mn–K catalyst. The results showed that treatments corn stalk with 0.4 MPa SE and alkali removed 84.16 wt% of hemicellulose and 71.83 wt% of lignin and thereby increased the cellulose content from 31.54 to 80.41 wt%. But the glucose loss was insignificant during pretreatment. Data from catalytic hydrogenolysis showed that pretreatment corn stalk with 0.4 MPa SE and alkali improved the yield of polyol, and about 20.38 wt% of ethylene glycol and 52.36 wt% of glycerol were produced after catalysis with Ni–W₂C/(coconut shell activated carbon, CSAC). Based on the yield of polyol, the catalytic performance of Ni–W₂C/CSAC was significantly better than those of Ni–W₂C/(coal-based activated carbon) and Fe–Mn–K/(amorphous carbon).

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1. Introduction

Nowadays, fossil energy depletion and climate deterioration are driving the development of alternative clean energy sources. Among various potential solutions, the converting of biomass into fossil fuels has been regarded as a promising alternative for sustainable production of biofuels and biochemicals (Binder and Raines, 2009). A critical step in corn stalk conversion into biochemical is of the production of polyol from biomass, which is affected by numerous factors such as the composition and structure of biomass, and type of pretreatment used. (Choi and Oh, 2012).

In recent years, many techniques including steam explosion (SE), liquid hot water extraction, alkaline hydrolysis, dilute-acid hydrolysis, ammonia treatment, and biological processes have been utilized

for pretreatment of lignocellulosic biomass (Çöpür et al., 2013; Du et al., 2013). Among these pretreatments, alkaline hydrolysis and SE techniques are in common (Kaushik and Singh, 2011; McIntosh and Vancov, 2011), which can effectively break down lignin seal, disrupt crystalline structure of cellulose and enhance opening up of the pretreated fibers to enzymatic digestion (Alvira et al., 2010).

The pretreatment of lignocellulose with SE was characterized by efficient separation of cellulose, reduced environmental pollution, and improving energy efficiency compared with other pretreatment methods (Hu et al., 2012). Alkaline treatment had a more effect on lignin solubilization and thereby increased the content of cellulose (Hendriks and Zeeman, 2009). Generally, lignin is thought to be a critical factor to inhibit catalytic hydrogenolysis by irreversible adsorption onto the catalyst. Nevertheless, SE in alkaline medium resulted in the hydrolysis of hemicellulose within the fiber and a cleavage of hemicellulose–lignin bond and then disrupted the crystalline structure of cellulose (Kaushik and Singh, 2011; Oliveira et al., 2013), rendering it more accessible to catalyst to allow more ready hydrogenation to polyol.

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The catalytic conversion of lignocellulose with catalyst has the unique advantages such as good selectivity and environmental friendliness (Zhao et al., 2010). Ideally, it is preferred to convert cellulose into fuels or chemicals in a single-step catalytic process. For such a one-step process, one of the main challenges is to search for a suitable catalyst that is able to promote hydrolysis, hydrogenolysis, and hydrogenation reactions. A representative example toward this direction was the one-step catalytic conversion of cellulose into polyols (Fukuoka and Dhepe, 2006; Irmak et al., 2013). Using Pt/Al₂O₃ and Ru/activated carbon as catalysts, they greatly increased the cellulose conversion and the yield of sugar alcohols. Ji et al. (2008, 2009) presented a combined catalytic, Ni–W₂C/activated carbon, for the conversion of cellulose to polyols, especially to ethylene glycol (EG). However, high production cost of pure cellulose and small pore size of catalyst particle were not conducive to large-scale trials and the reactants and/or reaction products transmission.

The objectives of this study were to investigate the effects of SE coupled with alkali on the structural feature, degradation pathway, product distribution and the thermal stability of corn stalk. Meanwhile, three catalysts were prepared and characterized and used to evaluate the efficiency of pretreatment by catalytic conversion of pretreated corn stalk into EG and glycerol.

2. Methods

2.1. Raw materials

Corn stalk used in this study was obtained from Yinchuan, China. It was chopped into approximately 1 cm pieces and milled using a fodder grinder. It was dried at 105 °C for 16 h, and then screened into powders of <80 mesh in size which was used as the raw material.

2.2. Pretreatment

2.2.1. SE

SE was carried out in a Zipper-clave autoclave. Samples of 10 g (oven dry) were treated for 1 h under 0.4 MPa, 0.6 MPa, and 0.8 MPa, respectively. The steam-exploded samples were filtrated using 80-mesh wire screen and collected.

2.2.2. Combination of SE and alkali

The steam-exploded solid samples were chemically treated with 5% (wt/wt) NaOH for 24 h at 60 °C, the solid–liquid ratio was 1:20 (wt/vol). After treatment, the mixture was filtered through paper fiberglass. The insoluble residue was washed with distilled water and dried at 105 °C for further catalytic hydrogenation test.

2.3. Catalytic hydrogenolysis

2.3.1. Pretreatment of carbon support

Three commercial carbon materials, coconut shell activated carbon (CSAC), coal-based activated carbon (CBAC), and amorphous carbon (AC) were used as the supports for catalyst preparation. In order to exclude any possible influence by the impurity metal on the commercial carbon support, all the carbon supports were treated with nitric acid solution (33 wt%) at 80 °C for 24 h prior to the deposition of active metal component.

2.3.2. Preparation of hydrogenolysis catalyst

The tungsten carbide catalyst was prepared using a method of carbothermal hydrogen reduction (CHR) (Sun et al., 2008). Both CSAC and CBAC were used as a carbon source, while ammonium

metatungstate (AM 30.0 wt%) and nickel nitrate (2.0 wt%) were used as the tungsten and nickel sources to produce Ni–W₂C/CSAC and Ni–W₂C/CBAC, respectively. Briefly, the carbon support was impregnated with an aqueous solution of AM and nickel nitrate by an incipient wetness method, and dried at 120 °C for 12 h. The resulting mixture was carburized in a hydrogen flow by a three-stage heating ramp: from room temperature to 400 °C at 5 °C min^{−1}, then to 700 °C at 1 °C min^{−1}, followed by holding at 700 °C for 1 h. Prior to exposure to air, the prepared carbide catalyst was passivated in a flow of 0.5% O₂/N₂ (30 mL min^{−1}) for 12 h at room temperature. The nominal weights loading of tungsten and nickel were 30 wt% and 2 wt%, respectively. In addition, a metal complex catalyst also was prepared by an impregnation method. It was defined as Fe (3 wt%)–Mn (1 wt%)–K (0.1 wt%)/AC.

2.3.3. Catalyst evaluation

The catalytic conversions of pure cellulose (Aladdin, microcrystalline with an average particle size of ≈90 μm. NO. CAS 9004-34-6) and pretreated corn stalk were performed in a stainless steel autoclave (Parr Instrument Company, 100 mL) at a H₂ pressure of 6 MPa and 245 °C for 2 h. For each reaction, 0.5 g of pure cellulose or pretreated corn stalk, 0.25 g catalyst, and 50 mL deionized water were charged into a reactor and stirred at a rate of 500 rpm. The polyols in reaction mixture were analyzed using high performance liquid chromatography (HPLC) (Fukuoka and Dhepe, 2006; Ji et al., 2008). The yield of polyol was calculated by the weight of polyol in the reaction mixture and cellulose put into the reactor (Ji et al., 2009). During the catalytic hydrogenolysis, the yields of EG and glycerol were calculated as follow formula:

$$\text{The wt\% of EG yield} = [(E \times V)/(P \times \omega)] \times 100 \quad (1)$$

$$\text{The wt\% of glycerol yield} = [(G \times V)/(P \times \omega)] \times 100 \quad (2)$$

where E (mg mL^{−1}) and G (mg mL^{−1}) represent EG and glycerol produced during catalysis, respectively. V = 50 mL, it represents the total volume of catalyst solution. P (mg) is the mass of raw materials, ω (wt%) represents the content of cellulose in corn stalk after pretreatment with alkali and SE. However, for the catalytic hydrogenolysis of microcrystalline cellulose, P = 500 mg, and ω = 1%.

2.4. Analytical methods

2.4.1. Chemical composition of corn stalk

All the treated and untreated samples were milled into 0.2 mm particles using the DFT-40 cutting mill. The contents of cellulose, hemicellulose, and lignin in sample were analyzed according to the procedures of the Van Soest method (Goering and Van Soest, 1970).

2.4.2. Determination of component after depolymerization

After pretreatment corn stalk with SE and alkali, the mixture was filtered through paper fiberglass. The solid phase was washed with distilled water and dried at 105 °C for determination the contents of cellulose, hemicellulose, lignin, and ash, while liquid phase was used to measure the sugar losses, degradation products and by-products. The contents of glucose, xylose, arabinose, acetic acid, and formic acid were determined by a HPLC method using a refraction index detector (Shimadzu, Japan) and an Aminex[®] HPX-87H Ion Exclusion column (HPLC Organic Acid Analysis Column) at 65 °C. Sulfuric acid (0.005 M) at flow rate of 0.6 mL min^{−1} was used as mobile phase, and the injection volume was 20 μL. The contents of furfural, 5-hydroxymethyl furfural (5-HMF), ferulic acid, p-coumaric acid, syringic aldehyde, 4-hydroxythylbenzoic acid, vanillin, syringic acid, and vanillic acid were determined by a HPLC method using a diode array detector (Shimadzu, Japan) and an InertSustain[®] C₁₈ column at 40 °C. Acetic acid (0.5 wt%) and methanol ratio of

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