Catalytic Hydrogenation of Corn Stalk to Ethylene Glycol and 1,2-Propylene Glycol

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ABSTRACT: The use of whole lignocellulosic biomass as the feedstock for cellulose conversion is of great significance for large-scale, low-cost biomass conversion to biofuel and other useful chemicals. We recently achieved the direct conversion of cellulose (pure microcrystalline cellulose) into ethylene glycol at high yields over tungsten carbide catalysts. Here, corn stalk, an agricultural residue available in large quantities, was used as a lignocellulosic feedstock for conversion over nickel-promoted tungsten carbide catalysts under hydrothermal conditions and a hydrogen atmosphere. Nine different pretreatment methods were employed to convert the raw corn stalk to cellulosic feedstock with different chemical components and structures before the catalytic reaction. We found that corn stalks pretreated with 1,4-butanediol, NaOH, H_2O_2, and ammonia produced much higher yields of ethylene glycol (EG) and 1,2-propylene glycol (1,2-PG) compared to raw corn stalks, whereas pretreatments with ethanol solution, hot water, hot limewater, and supercritical CO_2 just slightly improved the EG and 1,2-PG yields and corn stalk conversion. The hemicellulose in the corn stalk can be effectively converted to EG and 1,2-PG without hindering the cellulose conversion. In contrast, the lignin was resistant to degradation in the reaction and also inhibited EG and 1,2-PG production. The crystallinity of cellulose did not appear to have notable influence on the EG and 1,2-PG production. In view of the environmental benignity and low cost, pretreatment with ammonia and/or diluted H_2O_2 solution might be a practical method for corn stalk conversion, after which the derived cellulosic feedstock is readily converted into EG and 1,2-PG at an overall yield of 48% in the reaction.

1. INTRODUCTION

Lignocellulose is the most abundant source of biomass originating from plant photosynthesis in nature. Efficiently transforming lignocellulose into energy compounds and fine chemicals is of great significance for building a sustainable world. To date, extensive studies have been devoted to cellulose conversion by green and efficient ways, such as chemical and biological conversions using novel solid acid catalysts,[1−4] ionic liquids,[5−7] and enzymes.[8−13]

Recently, we achieved, for the first time, the direct catalytic conversion of cellulose into ethylene glycol (EG) over tungsten carbide catalysts.[14−17] Quite different from other studies where hexitols were the major products,[18−20] EG was the dominant product of cellulose conversion over our nickel-promoted tungsten carbide catalysts (Ni−W_2C/AC), with yields of 60−75 wt %. EG is an important bulk chemical (global production of ca. 18 million tonnes in 2007) for the synthesis of polymer fibers, resins, antifreezes, and so on.[21] Also, it can be used as a feed for H_2 production by catalytic reforming, as demonstrated by Dumesic et al.,[22] or for the synthesis of biodiesel.[23] EG is currently produced from ethylene oxide; thus, the direct catalytic conversion of cellulose to EG (DCE process) will contribute to a reduction of the dependence on nonrenewable petroleum and a lowering of the net emission of CO_2 to the environment. Furthermore, this process is highly atom-economic because most of the carbon atoms and hydroxyl groups from cellulose are well reserved in the products. Therefore, the DCE process is an ideal route for cellulosic biomass conversion, as well as for EG production.

However, as for many other pioneering studies in cellulose conversion,[18,19] the feedstock employed in our previous studies[14−17] was commercial pure microcrystalline cellulose, which was derived from lignocellulose after a series of complex pretreatments, involving pretreatments by acids, bases, and other chemicals. It is known that cellulose generally coexists with hemicellulose and lignin in raw lignocellulosic biomass. Using whole lignocellulosic biomass as the feedstock for cellulose conversion is of great significance for the survival of large-scale biomass conversion to useful chemicals. Although the influence of hemicellulose and lignin on the enzymatic conversion of cellulose has been studied in depth,[24−27] the mechanism and reaction conditions of the DCE process are quite different from those of biological conversions. Knowledge of the effects of multiple components in raw lignocellulosic biomass on the DCE process is highly desirable for overall biomass conversion.

Corn stock is a widely available agricultural residue that has great potential for use as a cellulosic feedstock for large-scale biomass conversion.[28] Herein, we employed corn stalk as a lignocellulosic feedstock and tested its performance in the DCE process with Ni−W_2C/AC catalysts. Nine different pretreatment methods on the raw corn stalk were employed to obtain cellulosic feedstocks with different components and structures. The influences of the composition, structure, and crystallinity of the cellulosic feedstock on the DCE process were studied in depth.

Table 1. Conditions and Severity Levels of Various Pretreatments

pretreatment method	conditions[a]	severity, log R_0[b]
ammonia and H_2O_2	15 wt % ammonia, 60 °C, 12 h followed with 2 wt % H_2O_2, 45 °C, 12 h	2.9
butanediol	1,4-butanediol, 200 °C, 4 h	5.3
NaOH	1 wt % NaOH, 60 °C, 12 h	1.6
H_2O_2	2 wt % H_2O_2, 45 °C, 12 h	1.2
ammonia	15 wt % ammonia, 60 °C, 12 h	1.6
50% ethanol	50% v/v ethanol aqueous solution, 120 °C, 4 h	2.9
hot water	water, 120 °C, 4 h	2.9
hot limewater	saturated limewater, 120 °C, 4 h	2.9
SC-CO_2	8 MPa CO_2, water, 150 °C, 4 h	3.8

[a] Weight ratios of corn stalk to the pretreating solutions were all 1:10, except for the pretreatments with hot water and SC-CO_2. For the hot water pretreatment, the weight ratio of corn stalk to water was 1:20. For the SC-CO_2 pretreatment, the weight ratio of corn stalk to SC-CO_2 was 1:4, in the presence of 10 wt % water (1 g of water/10 g of corn stalk). [b] Severity parameters involve factors of pretreatment time and temperature and are calculated by equation: log R_0 = log{time exp[(H − R)/14.75]}, where the units of pretreatment time are minutes, the units of pretreatment temperature (H) are °C, and R is the reference temperature (100 °C).[29]

2. MATERIALS AND METHODS

2.1. Corn Stalk and Pretreatment Methods. Corn stalk was obtained from Dalian, China. It was dried at 120 °C, milled, and screened into powders of <60 mesh in size. The pretreatment conditions are summarized in Table 1. The pretreatments with butanediol, 50% ethanol, hot water, hot limewater, and supercritical CO_2 (SC-CO_2) were conducted in a sealed batch reactor, whereas the others were performed in a three-mouth flask.

2.2. Analysis Methods. The components (cellulose, hemicellulose, and lignin) of raw and pretreated corn stalks were analyzed according to the procedures of the Van Soest method.[30] Each sample was analyzed twice to obtain an average value.

X-ray diffraction (XRD) patterns of samples were recorded on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm), operating at 40 kV and 40 mA. The crystallinity of the cellulose was determined in terms of the crystallinity index (CrI) according to the equation

$$CrI = 100 \times [(I_{002} - I_{amorphous})/I_{002}]$$

where I_{002} is the peak intensity of the crystalline portion of cellulose at about 2θ = 22.5° and $I_{amorphous}$ is the peak intensity of the amorphous portion of cellulose at about 2θ = 18.0°.[31]

To investigate composition changes in the corn stalk after various pretreatments, a Fourier transform infrared (FT-IR) spectroscopy system (Bruker Equinox 55 spectrometer) was used. In detail, samples diluted with KBr were pressed uniformly against the diamond surface using a spring-loaded anvil, and mid-IR spectra were obtained with an average of 120 scans from 4000 to 400 cm^{-1} at 4 cm^{-1} resolution.

The specific surface areas of raw and pretreated corn stalks were tested by N_2 adsorption at 77.3 K with a Micromeritics

ASAP 2010 Instrument. The morphology and microstructure of corn stalk before and after the pretreatments were observed by scanning electron microscopy (SEM) with an FEI Quanta 200 microscope operated in high vacuum and 20 kV. Before observation, the samples were sputter coated with a thin layer of gold.

2.3. Catalyst Preparation and Catalytic Conversion of Corn Stalk. The Ni−W_2C/AC catalysts were prepared by carbothemal reduction as described in ref 14. Typically, for 2% Ni−30% W_2C/AC catalyst, 2.0 g of activated carbon (Norit, surface area = 709 m^2/g) was impregnated with an aqueous solution containing 1.2 g of ammonium metatungstate and 0.3 of nickel nitrate and then dried at 120 °C for 12 h. The sample was carburized in H_2 flow with a three-stage heating ramp: from room temperature to 450 °C at 10 °C/min and then to 700 °C at 1 °C/min, with holding at this temperature for 1 h. Prior to exposure to air, the as-prepared carbide catalyst was passivated in a flow of O_2/N_2 (1% v/v) for 12 h at room temperature. By varying the nickel loading, 1% Ni−30% W_2C/AC, 2% Ni−30% W_2C/AC, 4% Ni−30% W_2C/AC, and 6% Ni−30% W_2C/AC catalysts were obtained.

The catalysts of 2% Ni/AC, 2% Pt/AC, and 2% Ru/AC were prepared by the incipient wetness impregnation method and reduced in H_2 at 450 °C for 1 h.

The catalytic conversion of corn stalk was carried out in a stainless-steel autoclave (Parr, 100 mL) with an initial H_2 pressure of 6 MPa and a temperature of 245 °C for 30−270 min. Typically, corn stalk (0.50 g), catalyst (0.15 g), and water (50 mL) were charged into the autoclave and stirred at a rate of 1000 rpm. After reaction, the liquid products were analyzed and quantified by high-performance liquid chromatography (HPLC; Agilent 1100), and the gas products were analyzed and quantified by gas chromatography (Agilent 6890N). The feedstock conversion was determined by the change in the feedstock weight before and after the reaction. The polyol yields and gas products were calculated by the equation yield (%) = [(number of moles of carbon in the polyol or gas)/(number of moles of carbon in the feedstock)] × 100%. The number of moles of carbon in the feedstock was determined by CHNS analyzer (Elementar Vario EL III).

3. RESULTS AND DISCUSSION

3.1. Analysis and Characterization of Raw and Pretreated Corn Stalks. First, we pretreated the raw corn stalk with nine different methods, namely, ammonia and H_2O_2, butanediol, NaOH, H_2O_2, ammonia, 50% ethanol, hot water, hot limewater, and SC-CO_2. The compositions of the raw and pretreated corn stalks are reported in Table 2. The raw corn stalk contained 33.1 wt % of water-soluble materials, which should be ascribed to monomeric sugars, various alditols, aliphatic acids, and inorganic ions.[32] The various pretreatments, in general, removed the major fraction of hemicellulose (25−77%) from the corn stalk. Especially for the pretreatments with butanediol and SC-CO_2, ca. 77% of the total hemicellulose was removed from the corn stalk.

Unlike for hemicellulose, the removal of lignin in the corn stalk was found to depend more on the properties of the treating solutions, but less on the severity level of the pretreatments. For instance, after treatment with hot water or SC-CO_2 (severity of ca. 3−4), very little lignin was removed, whereas in the basic or oxidative solutions such as the solutions of NaOH, H_2O_2, and ammonia (severity was ca. 1−2), 43−72% of lignin was removed. The pretreatment of butanediol was also very efficient to delignify corn stalk due to the good solubility of lignin in 1,4-butanediol.

Table 2. Composition of Corn Stalks after Different Pretreatments

sample no.	pretreatment method	severity, log R_0	soluble (%)	hemicell[a] (%)	cell[a] (%)	lignin (%)	ash (%)	dehemi[a,b] (%)	delig[a,c] (%)
A	ammonia and H_2O_2	2.9	6.1	14.8	72.4	6.2	0.5	48.6	74.9
B	butanediol	5.3	9.6	7.6	67.7	13.4	1.7	77.0	52.9
C	NaOH	1.6	4.8	17.2	69.1	8.4	0.5	51.7	72.4
D	H_2O_2	1.2	1.5	20.2	63.2	13.4	1.6	26.7	43.2
E	ammonia	1.6	2.1	18.5	71.3	7.6	0.6	30.7	67.0
F	50% ethanol	2.9	1.7	22.1	56.7	18.5	1.0	27.3	22.2
G	hot water	2.9	0.2	20.5	54.5	23.4	1.5	25.3	0.7
H	hot limewater	2.9	0.2	18.6	57.3	22.3	1.7	30.7	2.8
I	SC-CO_2	3.8	6.0	10.5	49.0	32.5	2.1	72.0	0
J	raw corn stalk	0	33.1	15.1	38.0	12.9	1.0	—	—

[a] Hemicell, cell, dehemi, and delig represent hemicellulose, cellulose, dehemicellulose, and delignin, respectively. [b] Dehemi (%) = {[percent of hemicellulose in raw corn stalk − (percent of hemicellulose in pretreated corn stalk × yield of pretreatment)]/(percent of hemicellulose in raw corn stalk)} ×100%. [c] Delig (%) = {[percent of lignin in raw corn stalk − (percent of lignin in pretreated corn stalk × yield of pretreatment)]/(percent of lignin in raw corn stalk)} ×100%.
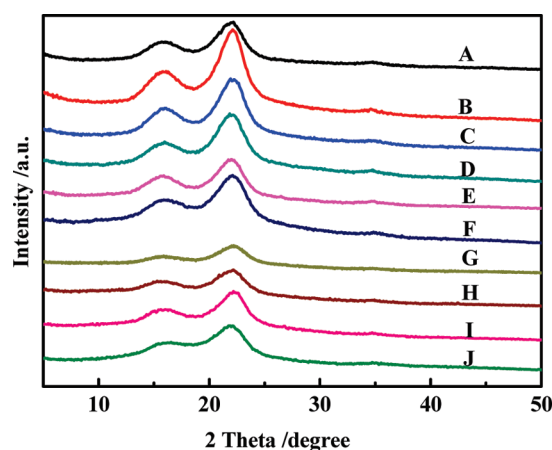

Figure 1. XRD patterns of raw and pretreated corn stalks: (A) ammonia and H_2O_2, (B) butanediol, (C) NaOH, (D) H_2O_2, (E) ammonia, (F) 50% ethanol, (G) hot water, (H) hot limewater, (I) SC-CO_2, (J) raw corn stalk.

The XRD patterns of raw and pretreated corn stalks are shown in Figure 1, and the derived crystallinity index values are listed in Table 3. The CrI values of the corn stalks after pretreatments with butanediol, NaOH, and H_2O_2 are 51.2, 49.6, and 45.7, respectively, notably higher than that of the raw corn stalk (CrI = 31.6). Some correlation can be found between the CrI and the composition of the corn stalk (Table 2), that is, the lower the contents of hemicellulose and lignin remaining in the corn stalk, the higher the CrI of cellulose obtained. This is consistent with the fact that the content of crystalline cellulose increases in the residual samples upon the removal of lignin, hemicellulose, and some less stable cellulose from corn stalk.[33,34]

The surface areas of the raw and pretreated corn stalks are in the range of 5−10 m^2/g (Table 3). Compared to the raw material, the surface areas of the corn stalks are nearly doubled by the pretreatments with NaOH and SC-CO_2, that is, ca. 10 m^2/g, whereas the surface areas are not changed much by the other pretreatments.

FT-IR spectra of raw and pretreated corn stalks are presented in Figure 2. The peak near 3348 cm^{-1} is attributed to the −OH stretching vibration from cellulose. The treatments with NaOH (spectrum C), ammonia (spectrum E), and hot limewater (spectrum H) caused significant reductions in the intensity of this peak compared to the other pretreatments, suggesting that the hydrogen bonds of cellulose were disrupted during the treatments with these basic solutions.[35]

The bands at 1745 and 1595 cm^{-1} are attributed to vibrations of the carbonyl group of the lignin side chain and the aromatic ring in lignin, respectively; their intensity decrease reflects the removal of lignin or the cleavage of lignin inside the chains.[29,33] After the pretreatments with 50% ethanol (spectrum F), hot water (spectrum G), hot limewater (spectrum H), and SC-CO_2 (spectrum I), the corn stalks retained the band intensities similar to that of the raw corn stalk. In contrast, the pretreatments with ammonia and H_2O_2, butanediol, NaOH, H_2O_2, and ammonia led to apparent reductions in the band intensity, suggesting that much of the lignin was removed from the corn stalks by these pretreatments. This is consistent with the results of the composition analysis of the pretreated corn stalks, as mentioned above.

SEM images of raw corn stalk and typical pretreated corn stalks are compared in Figure 3. At low magnification, no significant differences can be observed between the raw corn stalk and the corn stalk after pretreatments with ammonia and/or H_2O_2, suggesting that these pretreatments had little effect on the biomass morphology. However, the microstructure of corn stalk was found to be notably changed after other pretreatments, as shown in the SEM images obtained at higher magnification (Figure 3B,D,F,H). Many tiny pores were present on the sample surface, making it coarser than that of raw corn stalk. Particularly, after the pretreatment with ammonia and H_2O_2, bundles of microfibrils with porous surfaces were formed. This can be attributed to the removal of lignin, hemicellulose, and water-soluble materials from the corn stalk after the pretreatments.

3.2. Catalytic Conversion of Cellulosic Materials. *3.2.1. Catalyst Optimization.* To optimize the catalysts, the corn stalk treated with ammonia was used as a feedstock. Several typical hydrogenation catalysts including 2% Ni/AC, 2% Pt/AC, and 2% Ru/AC were tested and compared to the Ni−W_2C/AC catalysts in the reaction. As shown in Table 4 (entries 1−3), the classic hydrogenation catalysts of Ni/AC, Pt/AC, and Ru/AC did not give high yields of EG and 1,2-propylene glycol (1,2-PG). The overall yield of EG and 1,2-PG was less than 16%. Especially over the Ru/AC catalyst, no EG and 1,2-PG products were detected in

the aqueous solution. Almost all of the carbon was converted into gases, including methane (85.5% yield), ethane (11.6% yield, not listed in Table 4) and CO_2 (2.9% yield). This is consistent with the conversion results of pure microcrystalline cellulose reported previously.[16] The $Ni-W_2C/AC$ catalysts exhibited high yields of EG and 1,2-PG (entries 4−7). The best catalytic performance was obtained with the 2% $Ni-30\%$ W_2C/AC catalyst, over which EG and 1,2-PG were produced at yields of 18.3% and 13.9%,

Table 3. Crystallinity Index Values and Surface Areas of Corn Stalks before and after Pretreatments

pretreatment method	S_{BET} $(m^2\,g^{-1})$	CrI value	pretreatment method	S_{BET} $(m^2\,g^{-1})$	CrI value
ammonia and H_2O_2	5.6	48.4	50% ethanol	5.4	41.2
butanediol	5.4	51.2	hot water	7.4	39.0
NaOH	10.5	49.6	hot limewater	7.2	36.2
H_2O_2	4.9	45.7	$SC-CO_2$	9.9	43.0
ammonia	6.9	45.3	raw corn stalk	5.9	31.6
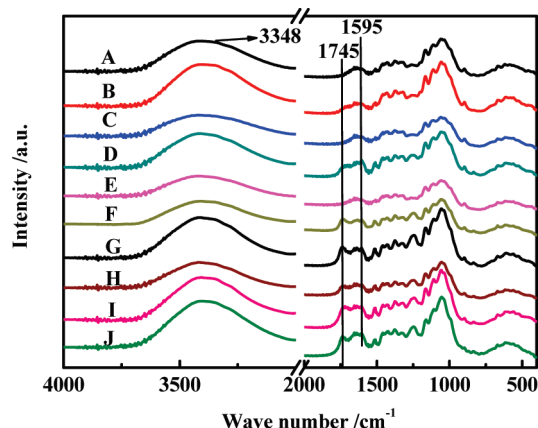
Figure 2. FT-IR spectra of raw and pretreated corn stalks: (A) ammonia and H_2O_2, (B) butanediol, (C) NaOH, (D) H_2O_2, (E) ammonia, (F) 50% ethanol, (G) hot water, (H) hot limewater, (I) $SC-CO_2$, (J) raw corn stalk.
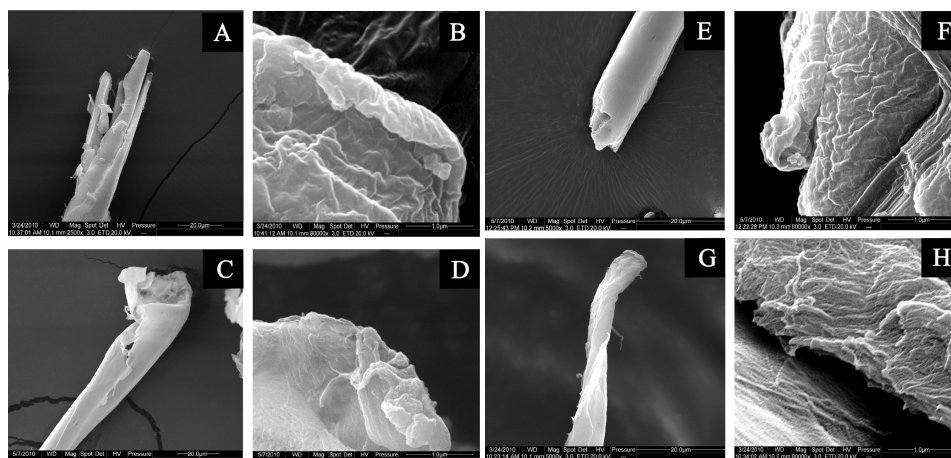
respectively, with 96.1% feedstock conversion. This is also consistent with our previous work,[14] where $Ni-W_2C/AC$ catalysts with different nickel loadings were examined for the conversion of pure microcrystalline cellulose. Thus, in the subsequent experiments, the 2% $Ni-30\%$ W_2C/AC was employed for the catalytic conversion of various cellulosic materials.

3.2.2. Comparison between Corn Stalk and Pure Cellulose Conversions. The catalytic performance of corn stalk was first compared with that of the pure microcrystalline cellulose (Table 4, entries 5, 8, and 9), and several notable differences were found. One is that the cellulosic corn stalk is not as readily converted as the pure cellulose. Even after 2 h of reaction, around 4% of the corn stalk remained, in contrast to the 100% conversion of pure cellulose in 30 min of reaction. This can be attributed to lignin remaining in the feedstock (7.5 wt % lignin contained in the pretreated corn stalk), which is hard to degrade completely.

Another difference lies in the yields of EG and 1,2-PG. The overall yield of EG and 1,2-PG was 33.2% in the corn stalk conversion, lower than the 58.0% yield (EG, 51.2%; 1,2-PG, 6.8%) obtained in the conversion of pure cellulose. Meanwhile, much more CO_2 gas was formed in the corn stalk conversion. The discrepancy demonstrates that the multicomponent feedstock is not only harder to degrade, but also less productive than the pure cellulose for EG and 1,2-PG production. The reaction time played an important role in the production of EG and 1,2-PG (as shown in Figure 4). The total yield of EG and 1,2-PG gradually rose to 35.4% in 150 min and leveled off at 38.4% when the reaction was prolonged to 270 min. Thus, the reaction time for the catalytic conversion of corn stalk with different pretreatments was set at 150 min in the subsequent experiments.

In addition, one can notice that more 1,2-PG was produced in the corn stalk conversion. The 1,2-PG yield was 13.9% (Table 4, entry 5), in contrast to 6.8% (Table 4, entry 9) in the case of pure cellulose conversion. This feature is discussed further in following sections. Evidently, the multiple components in the corn stalk have a notable impact on the corn stalk conversion and product distribution.

3.2.3. Influence of Various Pretreatments on Corn Stalk Conversion. The pretreatment process is one of the key and usually expensive steps for the efficient conversion of biomass.[37,38] For instance, many pretreatment methods have been investigated for cellulosic ethanol production.[39−41] The

Figure 3. SEM imagines of raw and typical pretreated corn stalks: (A,B) raw corn stalk, (C,D) ammonia pretreated, (E,F) H_2O_2 pretreated, (G,H) ammonia and H_2O_2 pretreated.

Table 4. Results of Catalytic Conversion of Cellulosic Materials over Various Catalysts[a]

sample no.	feedstock[b]	catalyst[c]	conv (%)	yield (%)							
				EG	PG	Xy	Man	Sor	CO	CO_2	CH_4
1	corn stalk	2% Ni	91.6	6.0	6.5	2.2	1.2	4.4	1.3	17.7	1.0
2	corn stalk	2% Pt	90.4	6.2	9.5	1.3	—	—	0.9	37.6	0.6
3	corn stalk	2% Ru	95.7	—	—	—	—	—	—	2.9	85.5
4	corn stalk	1% Ni−W_2C	94.7	9.0	8.0	2.3	—	—	1.0	25.2	0.5
5	corn stalk	2% Ni−W_2C	96.1	18.3	13.9	2.7	—	—	1.4	18.5	0.7
6	corn stalk	4% Ni−W_2C	91.7	10.3	12.8	—	—	—	0.9	23.2	1.4
7	corn stalk	6% Ni−W_2C	91.3	11.3	13.1	—	—	—	0.7	19.8	1.5
8	cellulose[d]	2% Ni−W_2C	100	55.3	8.4	—	1.8	3.7	0.5	3.6	—
9	cellulose	2% Ni−W_2C	100	51.2	6.8	—	1.1	2.6	1.2	5.7	0.5
10	xylose	2% Ni−W_2C	100	10.5	17.2	1.7	—	—	0.6	21.2	—
11	cellulose[e]	2% Ni−W_2C	100	46.4	7.4	—	1.7	4.2	1.4	5.9	0.8
12	cellulose and lignin	2% Ni−W_2C	99.5	13.1	4.2	—	1.6	2.8	1.3	18.0	—
13	cellulose and xylose	2% Ni−W_2C	100	43.2	10.3	1.3	2.2	7.1	0.6	7.9	—

[a] Typically, the reactions were conducted at 245 °C and 6 MPa H_2 for 2 h. Feedstock (0.5 g), catalyst (0.15 g), and water (50 mL) were put into a 100 mL stainless-steel autoclave. EG, PG, Xy, Man, and Sor represent ethylene glycol, 1,2-propylene glycol, xylitol, mannitol, and sorbitol, respectively. [b] The feedstock of entries 1−7 was corn stalk pretreated with ammonia; that of entries 8 and 9 was pure microcrystalline cellulose (Merk); that of entry 12 was a mixture of pure microcrystalline cellulose (Merck) and lignin (cellulose-to-lignin weight ratio of 5:1; lignin obtained by extracting corn stalk with high-boiling solvent, as in the literature method[36]); and that of entry 13 was a mixture of pure microcrystalline cellulose (Merck) and xylose with a weight ratio of 5:1. [c] W loadings were all 30 wt %, and all catalysts were supported on activated carbon (AC, Norit). [d] Reaction conducted for 30 min. Results cited from a previous work,[14] with polyol yields recalculated based on numbers of moles of carbon. [e] Cellulose (Merk) was pretreated with ball milling (Retsch, ZrO_2, 400 rpm, 4 h).
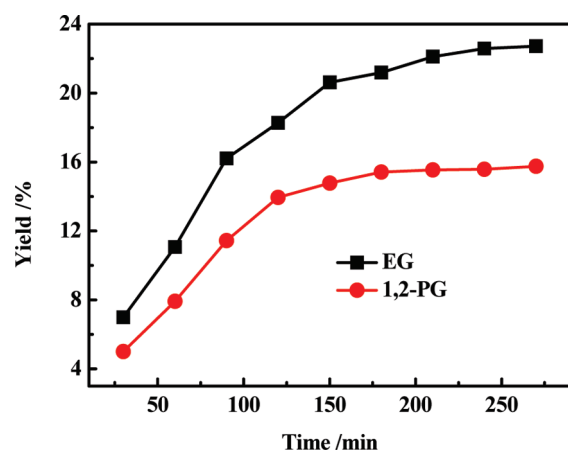

Figure 4. Effect of reaction time on yields of EG and 1,2-PG (feedstock, corn stalk pretreated with ammonia; catalyst, 2% Ni−30% W_2C/AC; temperature, 245 °C).

Figure 5. Catalytic performance of corn stalk after various pretreatments: (A) ammonia and H_2O_2, (B) butanediol, (C) NaOH, (D) H_2O_2, (E) ammonia, (F) 50% ethanol, (G) hot water, (H) hot limewater, (I) SC-CO_2, (J) raw corn stalk. (Reaction conditions: 2% Ni−30% W_2C/AC, 245 °C, 150 min.)

DCE process is quite different from the lignocellulose enzymatic conversions in respect of the operating conditions and reaction mechanism. Figure 5 presents the effects of various pretreatments on the catalytic conversion of corn stalks. Compared to the raw corn stalk, the pretreated corn stalks produced much higher EG and 1,2-PG yields in the reaction. Meanwhile, the feedstock conversions were markedly improved. Particularly, the pretreatments with ammonia and H_2O_2, NaOH, H_2O_2, and ammonia increased the overall yields of EG and 1,2-PG to 35−48% with ca. 95% conversion of feedstock, in contrast to the 3.3% overall yield of EG and 1,2-PG with 87.6% conversion for the raw corn stalk. The best catalytic performance was obtained for the corn stalk treated with ammonia and H_2O_2. Other pretreatments, including 50% ethanol, hot water, hot limewater, and SC-CO_2, also
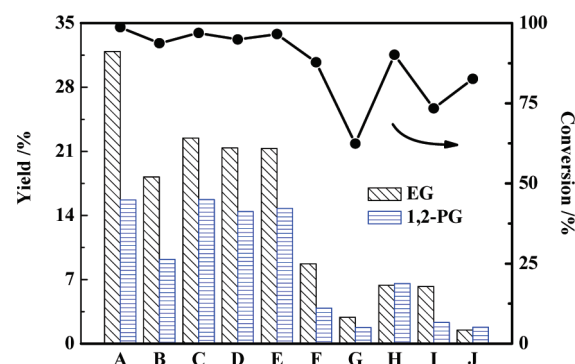
produced some positive effects on the EG and 1,2-PG production but not as markedly as the others. As shown in Table 2, the different pretreatments resulted in different compositions in the treated corn stalks. The common feature of the corn stalks after treatments with butanediol, NaOH, H_2O_2, and ammonia is that a large portion of lignin (43%−75%) was removed from the raw corn stalk. Meanwhile, the contents of cellulose increased to 60−70% after the pretreatments, in contrast to 38% cellulose in the raw material. However, the pretreatments with hot water, hot limewater, and SC-CO_2 removed only less than 5% lignin from the raw corn stalk. The yields of EG and 1,2-PG showed a reverse dependence on the lignin contents in the feedstock.

It has been reported that SC-CO_2-pretreated moisture lignocelluloses significantly increase the final yield of reducing sugar in enzymatic hydrolysis.[42,43] However, the similar pretreatment of

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dx.doi.org/10.1021/ie102505y |*Ind. Eng. Chem. Res.* 2011, 50, 6601−6608
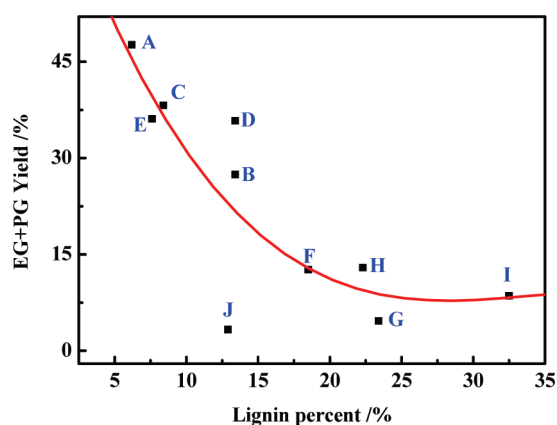
Figure 6. Plot of overall yields of EG and 1,2-PG as functions of lignin percent in corn stalks: (A) ammonia and H_2O_2, (B) butanediol, (C) NaOH, (D) H_2O_2, (E) ammonia, (F) 50% ethanol, (G) hot water, (H) hot limewater, (I) SC-CO_2, (J) raw corn stalk.

corn stalk in our study did not improve the EG and 1,2-PG yields or the corn stalk conversion, suggesting that the mechanisms of hydrothermal catalytic conversion and enzymatic conversion are quite different.

3.2.4. Influence of Lignin on the Cellulose Conversion. Among the nine different pretreatment methods, the pretreatment of corn stalk with SC-CO_2 removed most of the hemicellulose but left the lignin level nearly intact. In the catalytic conversion, the SC-CO_2-pretreated corn stalk was found to be as difficult as the raw corn stalk to convert to EG and 1,2-PG (Figure 5,I,J), suggesting that lignin might have major negative effects on the conversion of cellulosic biomass. Figure 6 demonstrates the negative effects of lignin on the polyol production more clearly. As shown in the plot of the overall yield of EG and 1,2-PG as a function of the lignin percentage in the corn stalk, when the lignin content increased from 6.2% to 18.5% in the pretreated corn stalks, the overall yield of EG and 1,2-PG decreased almost linearly from 47.6% to 12.8%. At lignin contents higher than 20%, the overall yield of EG and 1,2-PG leveled off as low as 10%.

To further examine the influence of lignin on the catalytic conversion of cellulose, pure microcrystalline cellulose and lignin were physically mixed at a weight ratio of 5:1 and tested in the reaction. The results (Table 4, entry 12) show that lignin addition apparently did not inhibit the cellulose conversion; however, it dramatically reduced the EG yield from 51.2% to 13.1%. Meanwhile, more gas products were formed, with a yield as high as 19.3%.

The marked decrease in EG yield might be related to lignin degradation during the catalytic reaction. Under hydrothermal or hydrogenolysis conditions, at least part of the lignin undergoes degradation and subsequent repolymerization.[44-47] By using gas chromatography/mass spectrometry analysis, we also found some typical lignin-degraded products, including lignin unit compounds (2-methoxyphenol, 4-ethylphenol, 2-methoxy-4-ethylphenol, 2,6-dimethoxypeneol, etc.) and long-chain alkanes in the liquid products of corn stalk conversion. The produced phenolic molecules and insoluble condensation products might not hinder the degradation of cellulose to small molecules, which mainly takes place over tungsten active sites,[16] but they might cover or poison the hydrogenation active sites of the catalyst and lead to a decrease of the EG and 1,2-PG yields.

3.2.5. Influence of Hemicellulose on the Cellulose Conversion. It was found that different pretreatments remove different amounts of hemicellulose content from corn stalks. Some of the resulting feedstock contained similar contents of lignin but different contents of hemicellulose. For instance, the corn stalk after pretreatments with ammonia or H_2O_2 contained more hemicellulose ($\sim$20 wt %, Table 2, entries D and E) than that obtained after the pretreatment with butanediol ($\sim$8 wt %, Table 2, entry B), although they all had similarly low contents of lignin (13 wt %). Thus, the influence of hemicellulose on the corn stalk conversion might be reflected in these cases. As shown in Figure 5, the 1,2-PG yields were $\sim$15% for the feedstocks with high hemicellulose contents (Figure 5D,E), in contrast to the $\sim$9% yield of 1,2-PG in the case of feedstock containing less hemicellulose (Figure 5B). On the other hand, the conversions of the three pretreated corn stalk samples were very similar. These results indicate that hemicellulose contributes to the formation of 1,2-PG and that it does not hinder the conversion of corn stalk in the reaction.

To further elucidate the hemicellulose performance, we employed pure xylose (the unit molecule of hemicellulose) as a feedstock for the conversion (Table 4, entry 10). After reaction, 1,2-PG and EG were produced in a yield ratio of 1.6:1, with complete conversion of xylose. A similar enhancement in the 1,2-PG yield was also observed when a mixture of cellulose and xylose (Table 4, entry 13) was used as the feedstock. As mentioned in our previous work,[16] glucose undergoes cracking reactions (such as retro-aldol condensation) over tungsten sites to form C_2 molecules, which are further hydrogenated into EG. Somewhat unlike glucose, we suggest here that xylose, a C_5 sugar, would be cracked into C_2 and C_3 intermediates, which eventually take part in EG and 1,2-PG formation. The high 1,2-PG yield in the conversion of pretreated corn stalks should be ascribed to the conversion of hemicellulose in the feedstock. The hemicellulose does not hinder the cellulose conversion. On the contrary, it is readily converted and contribute to the yields of 1,2-PG and EG.

3.2.6. Influence of Crystallinity and Surface Area on the Cellulose Conversion. The crystallinity index value of corn stalk was changed after the various pretreatment methods. Correlating the CrI values in Table 3 and the conversion results in Figure 5, one can notice that the EG and 1,2-PG yields in the catalytic conversion exhibited a positive correlation with the CrI values. To examine whether the crystallinity affects the catalytic conversion, we ball-milled (400 rpm, 4 h, PM100) microcrystalline pure cellulose (74.6% crystallinity) to low crystallinity (12.5%) and tested it in the reaction. However, the EG and 1,2-PG yields were not found to be changed significantly (EG, 46.4%; 1,2-PG, 7.4% vs EG, 51.2%; 1,2-PG, 6.8%; Table 4, entries 11 and 9). This result indicates that the crystallinity of cellulose does not play a critical role in the catalytic conversion to EG and 1,2-PG under the present experimental conditions. For the pretreated corn stalks with higher CrI values, the higher amount of cellulose but lower amounts of hemicellulose and lignin components will contribute to the EG and 1,2-PG production.

In addition, although the surface area of corn stalk was changed after some pretreatments (Table 3), no apparent relationship was found between the surface area and the corn stalk conversion.

4. CONCLUSIONS

In this study, we used corn stalks instead of pure cellulose as a whole biomass feedstock for the catalytic conversion of cellulose

into EG and 1,2-PG. Pretreatments of the corn stalk were found to be required for cellulose conversion with high yields of EG and 1,2-PG. The pretreatments of corn stalk with butanediol, NaOH, H_2O_2, and ammonia showed much better effects than those with 50% ethanol, hot water, hot limewater, and SC-CO_2 for the catalytic conversion of the resulting cellulosic materials.

The different catalytic performances of the corn stalks can be attributed to the change of components after the pretreatments. Lignin in the corn stalk markedly retarded the cellulose conversion and decreased the EG and 1,2-PG production. Hemicellulose in corn stalk can be effectively converted into 1,2-PG and EG without deteriorating the cellulose conversion. In addition, the crystallinity of the cellulosic feedstock did not exhibit a notable effect on the glycol formation in the catalytic conversion.

In view of their environmental benignity, low cost, and high efficiency, pretreatments with ammonia and/or diluted H_2O_2 might be suitable methods for delignifying corn stalk on a large scale. The derived cellulosic biomass can be readily converted to EG and 1,2-PG at an overall yield of 48% in the catalytic conversion.

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■ ACKNOWLEDGMENT

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dx.doi.org/10.1021/ie102505y |*Ind. Eng. Chem. Res.* 2011, 50, 6601–6608