Catalytic Conversion of Concentrated Miscanthus in Water for Ethylene Glycol Production

Jifeng Pang, Mingyuan Zheng, Aiqin Wang, Ruiyan Sun, Hua Wang, Yu Jiang, and Tao Zhang
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

DOI 10.1002/aic.14406

Miscanthus, a promising energy crop, was used for ethylene glycol (EG) production through one-pot catalytic conversion. With a binary catalyst composed of commercial tungstic acid and Raney Ni, the miscanthus with 1 % concentration was transformed into EG with a yield of 35.5%. However, the yield dropped to 13.6% as the miscanthus concentration was increased to 10 %. The underlying reason for the yield decrease was disclosed through analysis of the liquid products, investigation of pretreatments, and characterization of the catalysts. It was found that the protectors on the surface of miscanthus and the lignin component underwent decomposition under reaction conditions, resulting in the formation of some organic acids and unsaturated compounds that preferentially poisoned the Raney Ni catalyst and consequently decreased the EG yield. When the inhibitors were effectively removed by base solvent pretreatment, the EG yield was successfully improved to 39.0% even under 10% concentration of feedstock. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2254–2262, 2014

Keywords: miscanthus, concentrated, ethylene glycol, binary catalyst

Introduction

Recently, there has been growing interest in the production of biomass-derived chemicals.[1–3] Among various bioproducts, ethylene glycol (EG) is considered as one of the most important bulk chemicals. This valuable chemical has a huge global consumption, that exceeded 20 million tons in 2011, with a 5% annual increase during the past 5 years.[4] EG is mainly used for the synthesis of polyesters, such as poly(ethylene terephthalate), poly(ethylene naphthalate), and unsaturated polyester resin. It is also used as an antifreeze, solvent, and reductive agent.[5–7] EG is chiefly produced via hydration of ethylene oxide, which is petroleum dependent and neither sustainable nor environmentally benign. Therefore, it is desirable to produce EG from renewable biomass.

In 2008, we reported one-pot conversion of cellulose to EG over Ni-promoted tungsten carbide catalysts.[8,9] This is a highly atom-economic process because most of the C, H, and O atoms from biomass are theoretically reserved in the polyol products. The process opens a novel route for green EG production. On the basis of this work, by optimizing the structure of catalyst supports and understanding the reaction mechanism, we further developed a series of tungsten-based catalysts, over which the EG yield was enhanced to 75%, and the catalysts could be recycled over 20 times without deactivation.[10–13] Concurrently, Liu et al. developed a Ru/C-WO_3 catalyst to convert cellulose to EG with about 51% selectivity.[14] These works have paved a solid foundation for the potential industrial application for this process in the future.[15]

Cellulose has been regarded as a dominant substrate for the future biorefinery because its large-scale use does not threaten the food supply. However, it is difficult to obtain pure cellulose from raw lignocellulosic materials through simple and cheap pretreatment methods. In the raw biomass, cellulose usually coexists with hemicellulose and lignin. These components form complex three-dimensional structures with strong hydrogen bonds, which are difficult to separate using green and efficient methods.[16–18] Grassy biomass is the most abundant lignocellulosic materials because it is fast-growing and has a high productivity. However, compared with woody biomass, grassy biomass contains more miscellaneous components, such as water soluble compounds and minerals. These components could significantly reduce the catalytic conversion efficiency.[19] Previously, we reported that successive pretreatments of corn stalk with ammonia and hydrogen peroxide were required to obtain high EG yield.[20] The catalytic conversion of grassy biomass to EG with high efficiency and a simple procedure remains a challenge. The key factors determining the conversion efficiency for exploring the novel pretreatment methods and catalysts need to be studied.

One notable drawback of previous studies for biomass conversion is the low concentration of feedstock, which usually ranges from 1 to 3%.[8,14] From an industrial engineering viewpoint, this will lead to a diluted solution of final polyol products that augments the water and energy consumption for operation and products separation.[21–23] Therefore, using concentrated biomass as the feedstock is highly desirable for industrial applications. Under this feedstock condition, the

---

Correspondence concerning this article should be addressed to T. Zhang at taozhang@dicp.ac.cn.

influence of impurities in raw biomass on the EG yield must be investigated in detail and addressed clearly.

Miscanthus has attracted more and more attention as a promising energy crop. It is a perennial noninvasive grass with outstanding tolerance to cold and drought that requires little input but grows rapidly with a high yield (25 tons of dry weight biomass per hectare per year). Furthermore, its mineral content is very low. All of these features make miscanthus an ideal feedstock for biorefinery.[24–26] Herein, miscanthus was used as the feedstock for catalytic conversion to EG with a binary catalyst composed of cheap commercial tungstic acid and Raney Ni. The dominating factors affecting the EG selectivity were disclosed and a high EG selectivity was obtained under high feedstock concentration. This work should give valuable guidance to raw lignocellulosic biomass conversion.

Experimental

Miscanthus, pretreatment methods, and catalysts

Miscanthus was obtained from Hunan province, China. It was dried at 393 K, milled, and screened into powder with the size of <60 meshes. The solvents used in the pretreatments were methanol, ethanol, acetone, ethanol-ammonia, ammonia, and ethanol-NaOH. The weight ratio of solid to solvent was 1:10. The concentrations of ammonia and NaOH in liquid were 10 and 1 wt %. The pretreatments were conducted in a sealed batch reactor (Parr, 300 mL). Using the ethanol-NaOH pretreatment method as an example, 10 g miscanthus and 1 g NaOH were charged into the autoclave with 100 mL ethanol. Then, the autoclave was heated to 423 K and maintained for 2 h. After being cooled to room temperature, the miscanthus was filtered, washed, and dried at 393 K overnight.

Tungstic acid was purchased from Aladdin Chemistry Co., and Raney Ni was provided by GRACE Co.

Analysis methods

The main components (water soluble components, cellulose, hemicellulose, and lignin) of raw and pretreated miscanthus were analyzed according to the procedures of the Van Soest method.[27] 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 ($\lambda = 0.15432$ nm), operating at 40 kV and 40 mA. The crystallinity of cellulose in miscanthus was determined by crystallinity index (CrI) according to the following equation

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

where I_{002} is the peak intensity of the crystalline portion of the cellulose in miscanthus at $2\theta = 22.5°$ and $I_{\mathrm{amorphous}}$ is the peak intensity of the amorphous portion of the cellulose in miscanthus at $2\theta = 18.0°$.

To investigate the chemical composition changes of miscanthus before and after pretreatments, Fourier-transform infrared (FT-IR) spectra were recorded with a Bruker Equinox 55 spectrometer. In detail, the 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.

Thermogravimetric/differential thermal analyzer (TG/DTA) analysis of Raney Ni was carried out on a Setaram Setsys 16/18 analyzer (France) from 393 to 1173 K in an air flow of 25 mL/min at a heating rate of 10 K/min. Before analysis, the used Raney Ni was magnetically separated, washed 10 times with plenty of water, and dried at 393 K for 6 h.

The product solution and the compounds that strongly adsorbed on the Raney Ni catalyst in the conversion of concentrated miscanthus were analyzed with Gas chromatography–mass spectrometry (GC-MS) (Varian 450-GC, 320-MS) equipped with a Varian CP-WAX58 (FFAP) CB capillary column.Before analysis, the product solution and the used Raney Ni catalyst (water rinsed and dried) were extracted with cyclohexane and dichloromethane, respectively, for 30 min under ultrasonic conditions. The volume ratio of product solution to extracting solvent was 5:2, and the weight ratio of used Raney Ni to extracting solvent was 1:5.

The filtrates after the ethanol and ethanol-ammonia pretreatments of miscanthus were also analyzed with GC-MS. The solutions were diluted with an equal amount of ethanol before analysis.

The detailed GC-MS analysis conditions were as follows. The injector temperature was 523 K with a split ratio of 10:1. The GC oven temperature was maintained at 313 K for 3 min, and subsequently increased to 413, 428, and 533 K at a rate of 5, 2, and 10 K/min, respectively, and was finally maintained at 533 K for 10 min. The MS operating conditions were as follows. Ion source temperature, interface temperature, and quadrupole temperature were set at 503, 523, and 313 K, respectively. The electron ionization mode was set at 70 eV with a mass range of m/z 29–450. ChemStationTM software was used for data acquisition and the identifications of the compounds were acquired using a NIST Mass Spectral Library software (NIST 08, Software Version: 2.0 f) for correct matching.

Catalytic conversion of miscanthus

The catalytic conversion of miscanthus was carried out in a stainless-steel autoclave (Parr, 75 mL) with an initial H_2 pressure of 5 MPa (6 MPa for feedstock concentration higher than 6 wt %) at 518 K for 120 min. Typically, miscanthus, binary catalyst of tungstic acid and Raney Ni, and water were charged into the autoclave for reaction. Using 10% miscanthus conversion as an example, 2.78 g miscanthus, 0.33 g tungstic acid, 0.33 g Raney Ni (the ratio of tungstic acid and Raney Ni to reaction solution were both 0.12%), and 25 mL water were loaded in the autoclave and stirred at a speed of 800 rpm. After reaction, the liquid products were analyzed and quantified with High performance liquid chromatography (HPLC) (Agilent 1200, Shodex SC1011 packed column). The concentration of feedstock or catalysts was calculated by the following equation: concentration (wt %) = (weight of feedstock or catalyst) /(weight of feedstock + weight of water) × 100%. The feedstock conversions were determined by the change in feedstock weight before and after the reaction. The polyols yields were calculated by the following equation: yield (%) = (mole of carbon in the polyol)/(mole of carbon in feedstock) × 100%. The mole of carbon in the feedstock was determined by a CHNS element analyzer (Vario EL III, Element, Germany). The standard deviation of EG yield was less than 2%.

Results and Discussion

Chemical composition of raw and pretreated miscanthus

The contents of hemicellulose, cellulose, and lignin in miscanthus play a crucial role in optimizing strategies for biochemicals and biofuels production. Table 1 lists analysis results of the components and the elemental composition of hemicellulose, cellulose, and lignin in the raw and pretreated miscanthus. The raw miscanthus contains 5.3% water soluble components, 21.6% hemicellulose, 49.9% cellulose, and 15.9% lignin, corresponding to 47.3% C, 5.7% H, and less than 0.1% N as detected by element measurements. Notably, the miscanthus has a much lower content of water soluble components than corn stalk (5.3% vs. 33.1%),[20] and less lignin than woody biomass (15% vs. 25%).[28] This content might make it an ideal feedstock for the catalytic conversion to EG. After pretreatments of methanol, ethanol, and acetone, all of the miscanthus samples had similar carbon contents and distributions of hemicellulose, cellulose, and lignin. The removal of the water soluble components and partial removal of the lignin made the overall contents of hemicellulose and cellulose increase to 80%. Slightly different from the effects of neutral solvent pretreatments, base solvent pretreatments, such as ethanol-ammonia, ammonia, and ethanol-NaOH removed lignin much more effectively, leading to the lignin content and carbon content decreasing to less than 5 and 42–43%, respectively. These pretreatments also partially removed hemicellulose which has a strong interaction with lignin.[29] The overall content of hemicellulose and cellulose was increased to around 85% after base solvent pretreatments.

Crystallinity and structure analysis of raw and pretreated miscanthus

XRD and FT-IR are powerful methods to analyze the bulk and surface structure of lignocellulosic biomass, and have been extensively used for characterizing the raw and pretreated miscanthus. As shown in Figure 1, the CrI of raw miscanthus is 54.5, which is similar to grassy biomass, such as corn stalk, but much lower than that of woody biomass.[30] The CrI difference between grassy and woody biomass should be attributed to the diversity of growth period. A shorter growth period will result in imperfect crystalline structures of plants. After pretreatments of methanol, ethanol, and acetone, the CrI of the derived miscanthus samples was still levels off at 55, indicating that the organic solvent pretreatments did not change the crystalline structure of the raw miscanthus. Differently, after base solvent pretreatments, the peaks assigned to crystalline cellulose became sharp and intense, and the CrI increased from 54 to 58–62. The promoted crystallinity should be attributed to the increase of cellulose content in the biomass samples after the lignin component was removed by base solvent pretreatments.

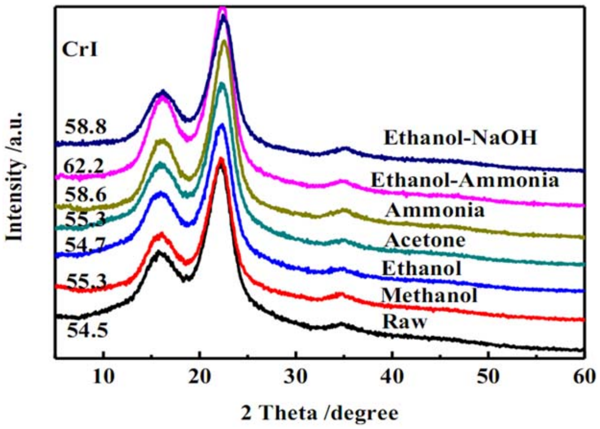


Figure 1. XRD patterns of the raw and pretreated miscanthus.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The chemical changes of the raw and pretreated samples were characterized with FT-IR. As shown in Figure 2, the surface chemical functional groups of miscanthus samples pretreated with low boiling point solvents, for example, methanol, ethanol, and acetone, are similar to that of the raw miscanthus. This result coincides well with the XRD characterization and composition analysis. Therefore, the low boiling point solvent pretreatment methods are relatively mild under the present conditions. They keep the structures of hemicellulose, cellulose, and lignin in the miscanthus intact. With base solvent pretreatments, the peak at 1732 cm^{-1} assigned to the carbonyl C=O stretch disappeared, suggesting that the base solvent pretreatments promote the cleavage of lignin side chains.[31] In addition, the bands at 1605, 1515, and 1270–1266 cm^{-1}, which could be associated with aromatic skeletal vibrations, aromatic skeletal vibrations plus C=O stretch, and guaiacyl ring plus C=O stretch, presented reduced intensities. This decrease in intensity implies that the lignin is largely removed from the miscanthus samples with the structure of the aromatic ring plus side chains being greatly destroyed.[32] Besides the removal of lignin, the bond around 3438 cm^{-1} assigned to O-H stretching is also greatly reduced after the ethanol-NaOH pretreatment, indicating that the hydrogen bonds of the cellulosic biomass are disrupted.[33]

Optimization of catalysts

It has been disclosed that the catalytic conversion of cellulose into EG over tungsten-based catalysts undergoes three sequential reaction steps.[10,12] First, the cellulose is hydrolyzed

Table 1. Composition of Raw and Pretreated Miscanthus

Pretreatment Methods	C (%)	H (%)	N (%)	Soluble (%)	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Ash (%)
Raw	47.3	5.7	<0.1	5.3	21.6	49.9	15.9	2.4
Ethanol	46.6	5.9	<0.1	2.8	29.6	51.5	11.6	2.3
Methanol	46.6	5.9	<0.1	2.2	32.0	50.1	11.3	2.9
Acetone	46.8	5.9	<0.1	3.0	29.6	51.0	10.7	3.1
Ethanol-Ammonia	42.8	6.1	<0.1	3.8	22.2	65.0	4.5	1.9
Ammonia	43.8	6.2	0.2	3.4	18.7	67.1	3.8	1.9
Ethanol-NaOH	43.1	6.1	<0.1	4.9	23.6	65.0	1.4	1.5

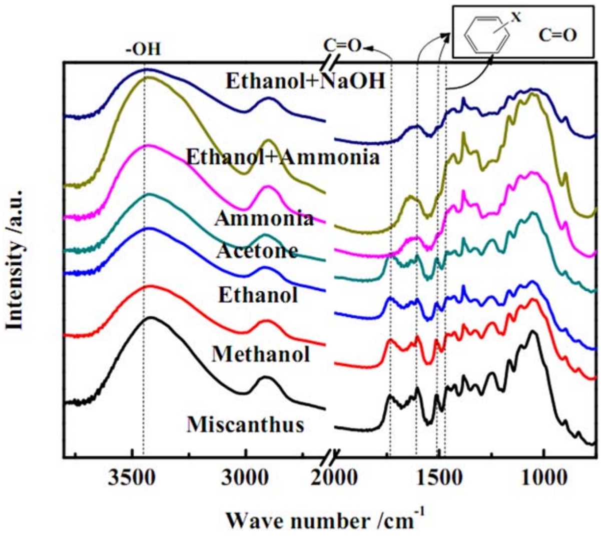


Figure 2. FT-IR spectra of the raw and pretreated miscanthus.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

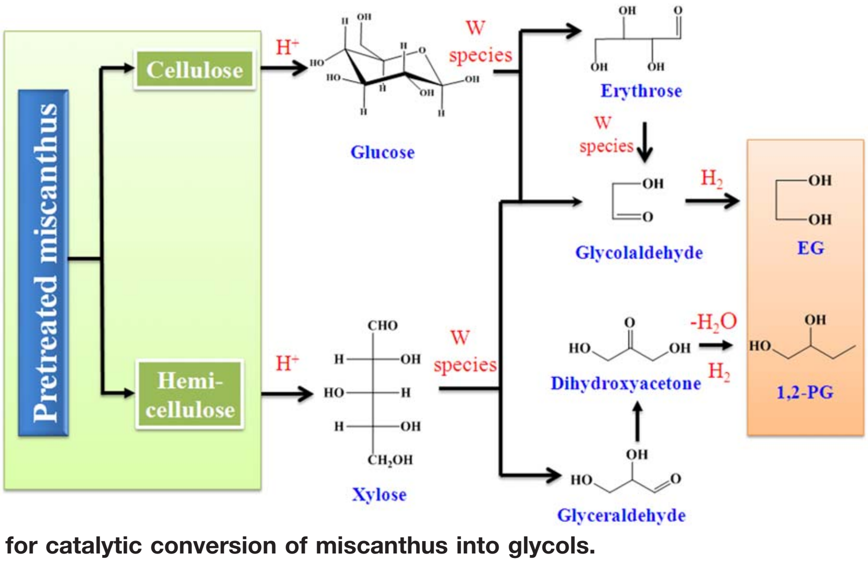
into oligosaccharides and glucose by catalysis of reversibly formed protonic acids in hot water.[34] Second, sugars are further catalytically degraded into glycolaldehyde over the tungsten sites via retro-aldol condensation. Third, the glycolaldehyde is hydrogenated into EG over the hydrogenation catalysts. A good balance between the sugar retro-aldol condensation and the intermediate hydrogenation is required to achieve a high EG selectivity in the cellulose conversion. For the conversion of lignocellulosic biomass, such as miscanthus (Scheme 1), both cellulose and hemicellulose are hydrolyzed, decomposed, and hydrogenated into glycols. Different from pure cellulose conversion, the main reaction intermediates of hemicellulose conversion are glycolaldehyde and glyceraldehyde, which can be further hydrogenated into EG and 1,2-PG, respectively. Therefore, the yield of 1,2-PG in the lignocellulose conversion is higher than that in the pure cellulose conversion.

Herein, commercial tungstic acid and Raney Ni were used as a binary catalyst for the miscanthus conversion. The best ratio of tungsten to nickel in the binary catalyst was first examined for the catalytic conversion of raw miscanthus. As shown in Figure 3A, at a fixed amount of Raney Ni (0.4%), the tungstic acid amount imposed a notably positive influence on the EG yield. For instance, the yields of EG and hexitols were 10.6 and 7.6%, respectively, in the absence of tungstic acid. With an increase in the amount of tungstic acid, the EG yield dramatically increased and then leveled off at around 30%. In contrast, the hexitols yields showed a reverse trend with the amount of tungstic acid, which decreased from 7.2 to 3.6%. This should be attributed to the competition between sugar hydrogenolysis and sugar hydrogenation.[35,36] Conversely, when the amount of tungstic acid was fixed at 0.12% as shown in Figure 3B, the EG yield initially increased and then decreased with the rise in the Raney Ni amount. The maximum EG yield reached 35.5% under the condition of 0.12% Raney Ni and 0.12% tungstic acid. This EG yield is remarkably higher than that obtained in the conversion of raw corn stalk (<10% EG yield) which is also a grassy biomass feedstock studied in our previous work.[20] Furthermore, the high yield of EG in the present study is comparable to or even better than that obtained in the conversion of woody biomass.[28] Thus, as a promising energy crop, miscanthus is very suitable for use as a biomass feedstock for the EG production.

Based on the result of catalyst optimization, we chose 0.12% tungstic acid and 0.12% Raney Ni as the typical catalyst composition for the conversion of miscanthus to EG.

Catalytic conversion of concentrated miscanthus

Because the reaction efficiency and the overall process sustainability of biomass conversion are highly dependent on the content of initial solid substrate,[37] we studied the catalytic conversion of miscanthus under high concentration conditions. As shown in Figure 4, when the concentration of the raw miscanthus was increased from 1 to 10%, the conversion of miscanthus remained above 90%. However, the EG yield decreased from 35.5 to 13.6% gradually. Although no miscanthus residue was observed in the autoclave after the reaction, there were humins and viscous oil floating on the surface of the solution or adhering to the autoclave. With HPLC analysis, we found that large amounts of organic acid



Scheme 1. Pathway for catalytic conversion of miscanthus into glycols.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

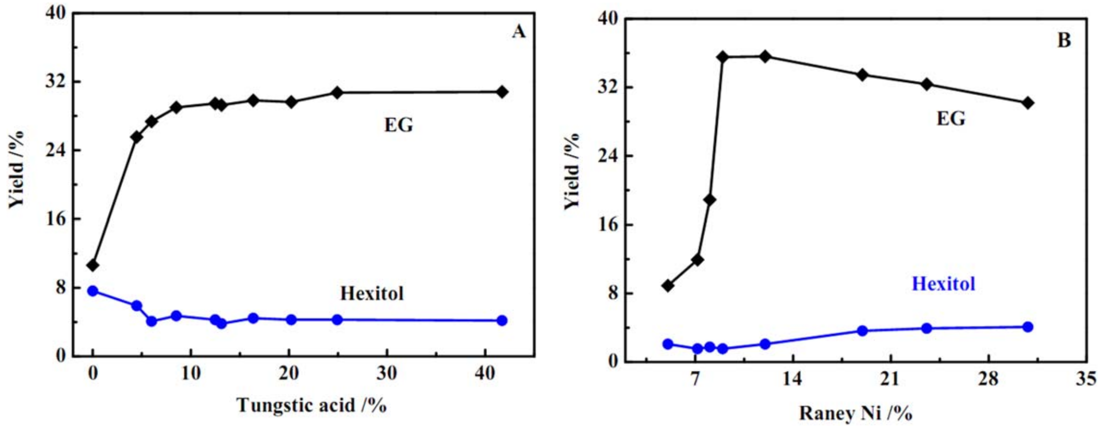


Figure 3. The influence of tungstic acid [(A) Raney Ni 0.4%] and Raney Ni [(B) Tungstic acid 0.12%] on the EG and hexitols yield (518 K, 120 min, and feedstock concentration was 1%).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and unknown compounds, as well as polyols, were present in the liquid products. GC-MS analysis (Figure 5A) further disclosed that plenty of long chain alkanes or acids (C16-C22) and lignin fractions were present in the product solution.

Influence of epidermal tissues on EG yield

One feature of grassy biomass is that it has some epidermal tissues covering the plant body such as epicuticular waxes, pectin substances, and fat acids. These protectors prevent plants from insect damage and make plants recalcitrant to degradation under natural conditions.[38,39] During the catalytic conversion of raw biomass, the sugar-based polymers including hemicellulose and cellulose will be efficiently degraded into monosaccharide and smaller molecules in the presence of catalysts under hydrothermal conditions. However, the epidermal tissues are reluctant to decompose but prone to aggregation, which might poison the catalysts and cause side reactions.

Considering that the epidermal tissues of lignocellulosic biomass are long chain organic compounds that are readily dissolved in organic solvents, we used methanol, ethanol, and acetone solvent pretreatments to remove the protectors from miscanthus. The advantage of the organic solvent pretreatments lies in the weak damage to the structure of lignocellulosic biomass, which reduces the hemicellulose loss and maximizes the global sugar content in the pretreated biomass. Furthermore, the solvents can be conveniently recovered by distillation, which is also feasible at the industrial scale.[40,41]

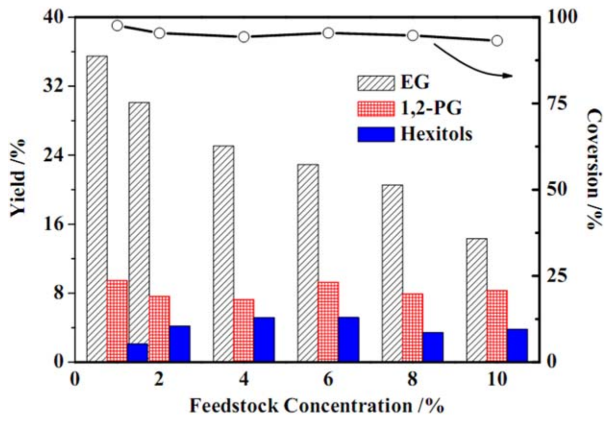


Figure 4. The influence of feedstock concentration on polyols yield (the concentrations of catalysts were increased proportionally).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

From the composition analysis, XRD and FT-IR spectra, we find that the pretreatments with low boiling point solvents did not change the structures of lignocellulosic biomass. The GC-MS analysis of the ethanol pretreated solution (Figure 5B) showed that long chain alkanes ($C_{18}H_{38}$, $C_{20}H_{42}$, $C_{21}H_{44}$), organic acids ($C_{16}H_{32}O_2$, $C_{18}H_{34}O_2$), and benzyl compound were present in the yellow solution. As previously reported, a large amount of surface protectors, such as cuticular wax (straight chain compounds and cyclic compounds), exist in the biomass and account for 10–50 μg/m^2.[42] These compounds are prone to dissolve in organic solvents at elevated temperatures. Therefore, the long chain alkanes and organic acids detected by GC-MS should be attributed to the surface protectors. In addition, because the lignin in grassy biomass is lowly polymerized, a small fraction of lignin would be degraded under pretreatment conditions. Therefore, the benzyl compounds should be attributed to the lignin degradation. Evidently, the organic solvent pretreatments effectively removed the surface protectors and partial lignin fractions.

The results of catalytic conversion of pretreated miscanthus under various concentrations are shown in Figure 6. Compared with the conversion of raw miscanthus at 1% concentration, the methanol, ethanol, and acetone pretreatment methods improved the EG yield from 35.5 to 39.5, 38.8 and 39.1%, respectively. Although increasing the concentration of feedstock to 10% led to a slight decrease of the EG yield to 25.8–27.3%, these values were at least twice that obtained with the concentrated raw miscanthus. As mentioned above, the difference between raw and low boiling point solvents pretreated miscanthus lies in the content of epidermal protectors. Thereby, the notably higher EG yield in the conversion of pretreated miscanthus should be attributed to the removal of the epidermal protectors of the biomass. Under a low concentration of feedstock, the content of epidermal protectors was too low to affect the EG yield. However, under 10% concentration of feedstock, both the amount of protectors and the interaction probability between epidermal protectors and catalysts or sugar intermediates were remarkably increased, leading to serious side reactions and poor EG

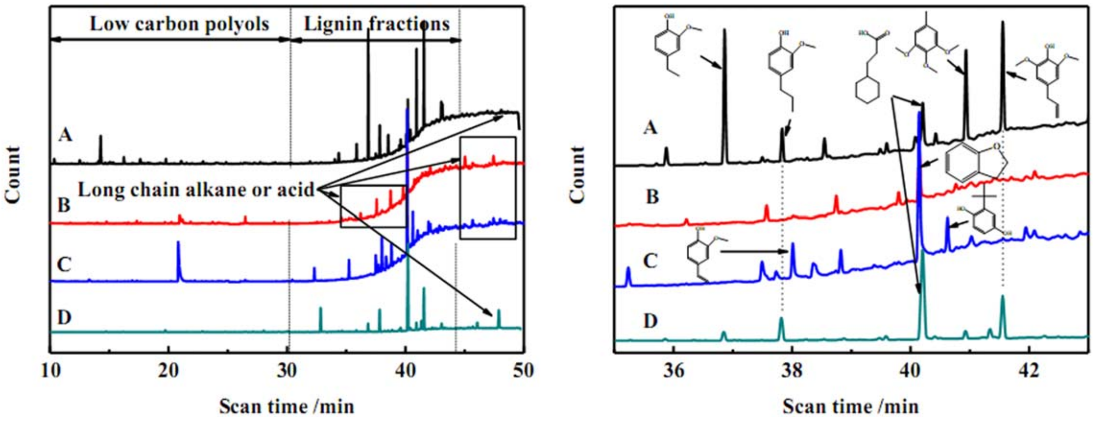


Figure 5. The whole (left) and partially magnified (right) GC-MS spectra of different liquid extractives. (A) Product solution was extracted with cyclohexane; (B) the filtered solution after ethanol pretreatment; (C) the filtered solution after ethanol-ammonia pretreatment; (D) Raney Ni was extracted with dichloromethane).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

selectivity. Therefore, the epidermal protector in the miscanthus is a key inhibitor that decreases the EG production.

Influence of lignin on EG yield

Lignin is the second most abundant component in lignocellulosic biomass. It has a rigid structure and strong bonds with hemicellulose and cellulose, which provide structural support and protection against plants pathogens. Thus, it is reluctant to degrade under enzymatic and chemical conditions.[43–45] Compared with the woody biomass, the lignin in the grassy biomass is lowly polymerized because of the short growth period. This makes it relatively active and apt to decompose into active fractions at high temperatures. Under hydrothermal conditions, these lignin fractions may self-polymerize or even react with unsaturated organic intermediates. Base pretreatment methods have been widely used to remove lignin from lignocellulosic biomass in the paper pulp industry. Herein, we used base and organic solvents pretreatment methods to remove lignin and addressed its influence on the EG yield.

As illustrated in the chemical analysis, XRD and FT-IR characterizations, base pretreatments remarkably changed the composition and structure of lignocellulosic biomass. Most of the lignin and a partial of the hemicellulose were removed. The black filtrate after ammonia pretreatment was analyzed with GC-MS. As shown in Figure 5C, a large amount of aromatic compounds were observed, which should be attributed to the derivatives of the lignin units. Under base and hydrothermal conditions, the C—O—C bonds among the lignin units were cleaved to form partially soluble compounds. In addition, some long chain alkanes were also found in the solution, which should be ascribed to the degradation of C—O—C or O=C—O—C bonds between lignin and some protectors under pretreated conditions.[46] Therefore, the ammonia or NaOH pretreatments greatly removed the lignin and the surface protectors of miscanthus.

For the catalytic conversion of miscanthus pretreated with base solvents, the EG yield was obtained as high as 45.5% under 1% concentration of feedstock (Figure 6). Even under 10% concentration of feedstock, the EG yields were retained at 36.4–40.0%, which was remarkably higher than that obtained with the raw miscanthus conversion (13.6% EG yield) or that with neutral organic solvents (25.8–27.3% EG yield). Meanwhile, no oils or humins were observed in the liquid products.

The base solvent pretreatment methods largely remove both epidermal protectors and lignin fractions. The improvement in

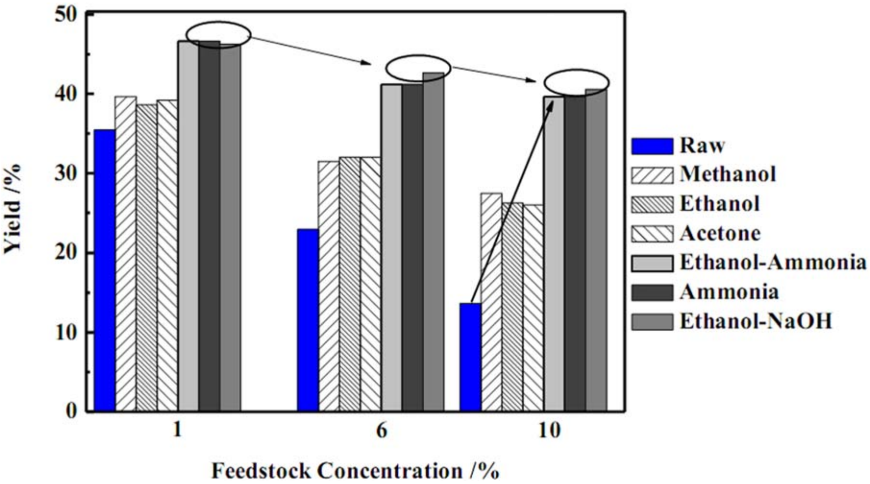


Figure 6. The influence of pretreatment methods on EG yield with different concentrations of feedstock.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

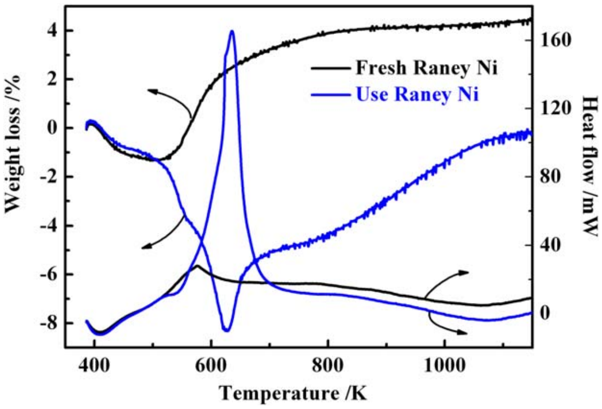


Figure 7. TG and heat flow curves of the fresh and used Raney Ni.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the EG yield demonstrates that the lignin has notably negative effects on the EG production, and it is another key inhibitor that decreases the EG production.

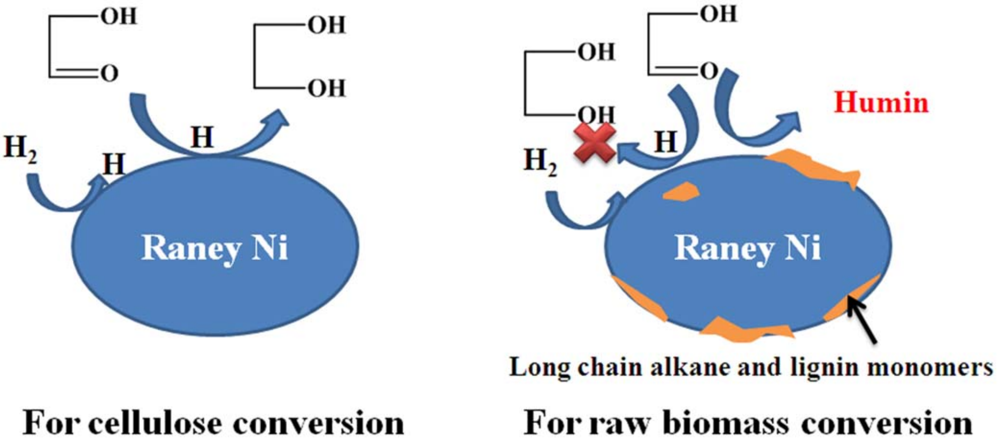
Essential reasons for the influence of epidermal tissues and lignin on EG yield

We have shown that epidermal tissues and lignin fractions in the miscanthus deteriorated the EG production, especially under a high concentration of feedstock. There are two reasons should be considered for this result, the interaction between the inhibitors and the sugar intermediates, and the poisonous effect of inhibitors on the catalysts.

Under the reaction conditions, the epidermal tissues and lignin fractions possibly react with active sugar intermediates and cause the EG yield to decrease. However, as there is no difference in the mass ratio of carbohydrates to epidermal tissues and lignin in the cases of different feedstock concentrations, the side reactions should take place to a similar extent. Therefore, there must be some other predominant factors affecting the EG selectivity.

In the present study, catalytic conversion of miscanthus, tungstic acid, and Raney nickel were used as a binary catalyst. To our knowledge, tungstic acid has a very low solubility in water at room temperature, but is more soluble at the reaction temperature of 518 K, thus forming a phase-transfer catalyst during the reaction.[12] This means that the catalytic performance of homogenous tungstic acid catalyst would be less possible to be affected by the compounds derived from degradation of epidermal tissues and lignin in the feedstock. However, for the heterogeneous catalyst Raney Ni, the case is quite different. The Raney Ni catalyst before and after the reaction were analyzed with TG/DTA. As shown in Figure 7, the weight loss of the fresh Raney Ni was 1.2% at 523 K, which should be attributed to the water desorption. At higher temperatures, the sample weight increased, which should be ascribed to the nickel oxidation. In contrast, the weight loss of the used Raney Ni reached 8.3% at 623 K, accompanied by a very sharp exothermic peak on the heat flow profile. This result indicates that some organic compounds were catalytically oxidized at this temperature. The content of the organic compounds in the used nickel catalyst was about 7%. Evidently, some organic compounds strongly adsorbed on the Raney Ni catalyst and could not be removed by 10-time water rinse before the TG/DTA experiment.

To further identify the compounds adsorbed on the catalysts, the used Raney Ni catalyst was extracted with dichloromethane, and the extractives were analyzed with GC-MS. As shown in Figure 5D, large quantities of organic compounds were detected in the extractives, including low carbon (C_3-C_6) alcohols, organic acids ($C_{16}H_{32}O_2$), and monophenolic compounds. Comparing the organic compounds adsorbed on the Raney Ni with the liquid products of the miscanthus conversion, we noticed that some organic acids and unsaturated compounds preferentially adsorbed on the surface of the Raney Ni. Obviously, the compounds adsorbed on the Raney nickel catalyst occupy the active sites and retard the hydrogenation of other reactants. During the catalytic conversion of cellulose to EG, the intermediates such as derived sugars and glycolaldehyde need to be further hydrogenated into polyols over nickel sites. Otherwise, these unsaturated compounds undergo further degradation or polymerization to form polymers and humins (Scheme 2). Therefore, we concluded that the deactivation of Raney nickel by the compounds derived from epidermal tissues and lignin in miscanthus is the reason for the decrease in EG yield, particularly under a high concentration of feedstock.



Scheme 2. Scheme of catalyst deactivation with raw lignocellulosic biomass as the feedstock.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

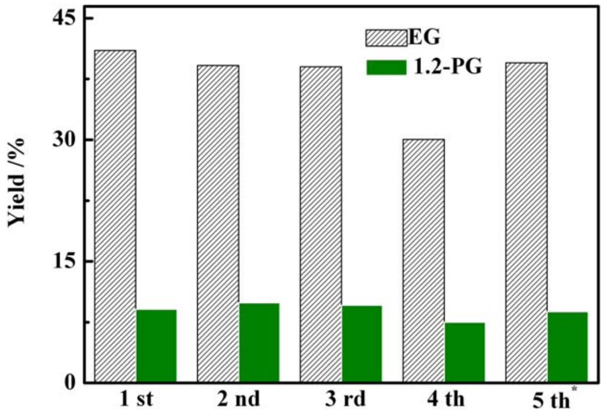


Figure 8. The reusability of binary catalysts in miscanthus conversion (Miscanthus-Ethanol-NaOH: 2.78 g, Raney Ni: 0.33 g, tungstic acid: 0.33 g; H_2O: 25 mL, 518 K, 2 h, 6 MPa H_2; *:0.05 g tungstic acid was added for the fifth reaction).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As the strong adsorption of large molecule organic compounds on Raney Ni was the essential reasons for the decrease in EG yield, we rinsed the used Raney Ni with plenty of ethanol after magnetical separation and used it again in combination with tungstic acid that was recycled by filtration for the next run. As shown in Figure 8, the as-recycled binary catalyst afforded an EG yield up to 30.1% in the subsequent second and third runs when Ethanol-NaOH pretreated miscanthus was used as the feedstock. The slight decrease in EG yield in the fourth run was attributed to the accumulated leaching of tungstic acid to the liquid. After supplementing 0.05 g of tungstic acid, the EG yield was recovered to 39.5% in the fifth runs.

Conclusions

Miscanthus is an ideal cellulosic feedstock for the catalytic conversion to produce EG. It contains fewer of water soluble compounds and lignin compared with corn stalk and woody biomass. With a binary catalyst of commercial tungstic acid and Raney Ni, 35.5% EG yield was obtained in the raw miscanthus conversion.

Increasing the concentration of raw miscanthus greatly decreased the EG yield. Two inhibitors that decrease the EG yield are the protectors on the surface of the biomass and the lignin component in the miscanthus. The degraded components from epidermal issues and the lignin of miscanthus strongly occupied the active sites of Raney Ni, caused remarkable side reactions, and consequently decreased the EG yield. By pretreating miscanthus with base solvents, the inhibitors were effectively removed and the EG yield was successfully improved to 39% even under 10% concentration of feedstock.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (21176235, 21306191, and 21376239) and 973 program of China (2009CB226102). The authors thank Prof. Tao Sang (Institute of Botany, Chinese Academy of Sciences, 20 Nanxincun, 100093 Beijing, People's Republic of China) for providing miscanthus samples.

Literature Cited

1. Corma A, Iborra S, Velty A. Chemical routes for the transformation of biomass into chemicals. *Chem Rev*. 2007;107:2411–2502.
2. Ruppert A, Weinberg K, Palkovits R. Hydrogenolysis goes bio: from carbohydrates and sugar alcohols to platform chemicals. *Angew Chem Int Ed*. 2012;51:2564–2601.
3. Zhou C, Xia X, Lin C, Tong D, Beltramini J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem Soc Rev*. 2011;40:5588–5617.
4. Yue H, Zhao Y, Ma X, Gong J. Ethylene glycol: properties, synthesis, and applications. *Chem Soc Rev*. 2012;41:4218–4244.
5. Hagiopol C. *Copolymerization: Toward a Systematic Approach*. New York: Kluwer Academic, 1999.
6. Song Q, Wang F, Xu J. Hydrogenolysis of lignosulfonate into phenols over heterogeneous nickel catalysts. *Chem Commun*. 2012;48: 7019–7021.
7. Yin J, Wang J, Li M, Jin C, Zhang T. Iodine ions mediated formation of monomorphic single-crystalline platinum nanoflowers. *Chem Mater*. 2012;24(14):2645–2654.
8. Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, Chen J. Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts. *Angew Chem Int Ed*. 2008;47:8510–8515.
9. Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, Shu Y, Stottlemyer A, Chen J. Catalytic conversion of cellulose into ethylene glycol over supported carbide catalysts. *Catal Today*. 2009;147: 77–85.
10. Zheng M, Wang A, Ji N, Pang J, Wang X, Zhang T. Transition metal-tungsten bimetallic catalysts for the conversion of cellulose into ethylene glycol. *ChemSusChem*. 2010;3:63–66.
11. Zhang Y, Wang A, Zhang T. A new 3D mesoporous carbon replicated from commercial silica as a catalyst support for direct conversion of cellulose into ethylene glycol. *Chem Commun*. 2010;46:862–864.
12. Tai Z, Zhang J, Wang A, Zheng M, Zhang T. Temperature-controlled phase-transfer catalysis for ethylene glycol production from cellulose. *Chem Commun*. 2012;48:7052–7054.
13. Tai Z, Zhang J, Wang A, Pang J, Zheng M, Zhang T. Catalytic conversion of cellulose to ethylene glycol over a low-cost binary catalyst Raney Ni and tungstic acid. *ChemSusChem*. 2013;6:652–658.
14. Liu Y, Luo C, Liu H. Tungsten trioxide promoted selective conversion of cellulose into propylene glycol and ethylene glycol on a ruthenium catalyst. *Angew Chem Int Ed*. 2012;51:3249–3253.
15. Wang A, Zhang T. One-pot conversion of cellulose to ethylene glycol with multifunctional tungsten-based catalysts. *Acc Chem Res*. 2013;46(7):1377–1386.
16. Ragauskas A, Williams C, Davison B, Britovsek G, Cairney J, Eckert C, Frederick W Jr, Hallett J, Leak D, Liotta C, Mielenz J, Murphy R, Templer R, Tschaplinski T. The path forward for biofuels and biomaterials. *Science*. 2006;311:484–489.
17. Matson T, Barta K, Iretskii A, Ford P. One-pot catalytic conversion of cellulose and of woody biomass solids to liquid fuels. *J Am Chem Soc*. 2011;133:14090–14097.
18. Hu F, Ragauskas A. Pretreatment and lignocellulosic chemistry. *Bioenergy Res*. 2012;5:1043–1066.
19. Himmel M, Ding S, Johnson D, Adney W, Nimlos M, Brady J, Foust T. Biomass recalcitrance: engineering plants and enzymes for biofuels production. *Science*. 2007;315:804–807.
20. Pang J, Zheng M, Wang A, Zhang T. Catalytic hydrogenation of corn stalk to ethylene glycol and 1,2-propylene glycol. *Ind Eng Chem Res*. 2011;50:6601–6608.
21. Liang G, Wu C, He L, Ming J, Cheng H, Zhuo L, Zhao F. Selective conversion of concentrated microcrystalline cellulose to isosorbide over Ru/C catalyst. *Green Chem*. 2011;13:839–842.
22. Luterbacher J, Chew Q, Li Y, Tester J, Walker L. Producing concentrated solutions of monosaccharides using biphasic CO2–H2O mixtures. *Energy Environ Sci*. 2012;5:6990–7000.
23. Xiao Z, Jin S, Pang M, Liang C. Conversion of highly concentrated cellulose to 1, 2-propanediol and ethylene glycol over high efficient CuCr catalysts. *Green Chem*. 2013;15:891–895.
24. Somerville C, Youngs H, Taylor C, Davis S, Long S. Feedstocks for lignocellulosic biofuels. *Science*. 2010;329:790–792.
25. Sang T, Zhu W. China's bioenergy potential. *GCB Bioenergy*. 2011; 3:79–90.

26. Brosse N, Dufour A, Meng X, Sun Q, Ragauskas A. Miscanthus: a fast-growing crop for biofuels and chemicals production. *Biofuels Bioprod Bioref.* 2012;6:580–598.
27. Goering H, Van Soest P. *Forage Fiber Analysis. USDA-ARS Agriculture Handbook 379*. Washington, DC: U.S. Government Printing Office, 1970:12–20.
28. Li C, Zheng M, Wang A, Zhang T. One-pot catalytic hydrocracking of raw woody biomass into chemicals over supported carbide catalysts: simultaneous conversion of cellulose, hemicellulose and lignin. *Energy Environ Sci*. 2012;5:6383–6390.
29. Sierra R, Holtzapple M, Granda C. Long-term lime pretreatment of poplar wood. *AIChE J*. 2011;57:1320–1328.
30. Nitsos C, Matis K, Triantafyllidis K. Optimization of hydrothermal pretreatment of lignocellulosic biomass in the bioethanol production process. *ChemSusChem.* 2013;6:110–122.
31. Kumar R, Mago G, Balan V, Wyman C. Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies. *Bioresour Technol.* 2009;100: 3948–3962.
32. Pang C, Xie T, Lin L, Zhuang J, Liu Y, Shi J, Yang Q. Changes of the surface structure of corn stalk in the cooking process with active oxygen and MgO-based solid alkali as a pretreatment of its biomas conversion. *Bioresour Technol.* 2012;103:432–439.
33. Kumar R, Mago G, Balan V, Wyman C. Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies. *Bioresour Technol.* 2009;100: 3948–3962.
34. Luo C, Wang S, Liu H. Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water. *Angew Chem Int Ed.* 2007;46:7636–7639.
35. Pang J, Wang A, Zheng M, Zhang Y, Huang Y, Chen X, Zhang T. Catalytic conversion of cellulose to hexitols with mesoporous carbon supported Ni-based bimetallic catalysts. *Green Chem.* 2012;14:614–617.
36. Wu Z, Ge S, Ren C, Zhang M, Yip A, Xu C. Selective conversion of cellulose into bulk chemicals over Brønsted acid-promoted ruthenium catalyst: one-pot vs. *sequential process. Green Chem.* 2012;14: 3336–3343.
37. Román-Leshkov Y, Barrett C, Liu Z, Dumesic J. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature.* 2007;447:982–985.
38. Zhao X, Zhang L, Liu D. Biomass recalcitrance. Part I: the chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocelluloses. *Biofuels Bioprod Bioref.* 2012;6:465–482.
39. Duarte G, Moreira L, Jaramillo P, Filho E. Biomass-derived inhibitors of holocellulases. *Bioenergy Res.* 2012;5:768–777.
40. Serrano L, Egües I, Alriols M, Llano-Ponte R, Labidi J. Miscanthus sinensis fractionation by different reagents. *Chem Eng J*. 2010;156: 49–55.
41. Wang K, Yang H, Guo S, Tang Y, Jiang J, Xu F, Sun R. Organosolv fractionation process with various catalysts for improving bioconversion of triploid poplar. *Process Biochem.* 2012;47:1503–1509.
42. Buschhaus C, Jetter R. Composition differences between epicuticular and intracuticular wax substructures: how do plants seal their epidermal surfaces? *J Exp Bot*. 2011;62(3):841–853.
43. Hansen M, Kristensen J, Felby C, Jørgensen H. Pretreatment and enzymatic hydrolysis of wheat straw (Triticum aestivum L.)-the impact of lignin relocation and plant tissues on enzymatic accessibility. *Bioresour Technol.* 2011;102:2804–2811.
44. Wang X, Rinaldi R. Solvent effects on the hydrogenolysis of diphenyl ether with Raney nickel and their implications for the conversion of lignin. *ChemSusChem.* 2012;5(8):1455–1466.
45. He J, Zhao C, Lercher J. Ni catalyzed cleavage of aryl ethers in aqueous phase. *J Am Chem Soc*. 2012;134(51):20768–20775.
46. Fang X. Chemical composition of soybean root epidermal cell walls. MSc Thesis. Waterloo, ON, Canada: University of Waterloo, 2006.

Manuscript received April 1, 2013, and revision received Jan. 24, 2014.