DOI: 10.1002/cssc.201100745

Acid-Catalyzed Conversion of Xylose in Methanol-Rich Medium as Part of Biorefinery

Xun Hu, Caroline Lievens, and Chun-Zhu Li*[a]

Acid treatments of xylose have been performed in a methanol/water mixture to investigate the reaction pathways of xylose during bio-oil esterification. Xylose was mainly converted into methyl xylosides with negligible humins formed below 130 °C. However, humins formation became significant with the dehydration of xylose to furfural and 2-(dimethoxymethyl)furan (DOF) at elevated temperatures. The conversion of xylose to methyl xylosides protected the C1 hydroxyl group of xylose, which stabilized xylose and suppressed the formation of sugar oligomers and polymerization reactions. In comparison, the conversion of furfural to DOF protected the carbonyl group of furfural. However, the protection did not remarkably suppress the polymerization of furfural at high temperatures because of the shift of the reaction equilibrium from DOF to furfural with a prolonged residence time. In addition, the acid treatment of furfural produced methyl levulinate in methanol and levulinic acid in water, which was catalyzed by formic acid.

Introduction

Flash pyrolysis of biomass produces a bio-oil that has been recognized as a potential fuel and chemical feedstock.[1–3] However, the raw bio-oil cannot be directly used because of its intrinsic deleterious properties such as corrosiveness and thermal instability.[4,5] Esterification can overcome the undesirable properties by removing the organic acids in bio-oil with alcohols.[6] In addition to organic acids, carbohydrates are another main component of bio-oil.[7,8] The presence of carbohydrates increases not only the viscosity but also the instability of bio-oil as carbohydrates have a high tendency to polymerize.[9–12] Thus, the reaction pathways of carbohydrates in the esterification of bio-oil are of concern.

The simple carbohydrates in bio-oil mainly refer to the C6 and C5 carbohydrates, which originate from the degradation of cellulose and hemicelluloses in biomass. Acid treatments of the C6 or C5 carbohydrates in water have been intensively investigated,[13–15] and the conversion of the C6 carbohydrates in methanol has also been investigated recently.[16–18] However, few studies focused on the conversion of the C5 carbohydrates in methanol-rich media, the understanding of which helps us to elucidate the catalytic behavior of the C5 carbohydrates in bio-oil esterification and to select appropriate conditions to avoid side reactions.

In water, it is known that the acid treatment of C5 carbohydrates such as xylose, a typical C5 carbohydrate from the degradation of hemicellulose, produces furfural.[19] In methanol and in the presence of acids, it is known that xylose can be converted to methyl xylosides;[20] however, further conversion of methyl xylosides in methanol is not understood. In addition, both xylose and furfural have a high tendency to polymerize in acidic aqueous media.[21,22] Polymerization is undesirable as it diminishes the utilization efficiency of xylose and may lead to catalyst deactivation. Hence, a question is raised. Does a methanol-rich medium suppress the polymerization of xylose and furfural? Moreover, does a methanol-rich medium change the degradation pathways of xylose and furfural? These are the key questions that we have tried to answer in this study. Xylose was used as the model compound of C5 carbohydrates. A methanol/water mixture was used as the reaction medium as water is invariably present in bio-oil. Amberlyst 70, which is a commercial solid acid catalyst, was used to catalyze the conversion of xylose in the methanol/water mixture.

Results and Discussion

Effects of reaction temperature on the conversion of xylose in methanol/water medium

Xylose conversion, product distribution, and humins formation at the temperatures from 90 to 170 °C are depicted in Figure 1. The required reaction temperature was reached at 0 min on the *x*-axes of the graphs in Figure 1. Prolonged reaction time and increased temperature promote the conversion of xylose, as shown in Figure 1a. Methanolysis of xylose dominated below 130 °C, producing methyl-α-D-xylopyranoside (MAXP, Figure 1b) and methyl-β-D-xylopyranoside (MBXP, Figure 1c) as the main products and methyl-α-D-xylofuranoside (MAXF) and methyl-β-D-xylofuranoside (MBXF) as minor products. MAXF and MBXF are not presented, as their concentrations were low and became negligible with the progress of the reaction. The

[a] Dr. X. Hu, Dr. C. Lievens, Prof. C.-Z. Li
Fuels and Energy Technology Institute
Curtin University of Technology
GPO Box U1987, Perth, WA 6845 (Australia)
Fax: (+61) 8-9266-1138
E-mail: chun-zhu.li@curtin.edu.au

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201100745.

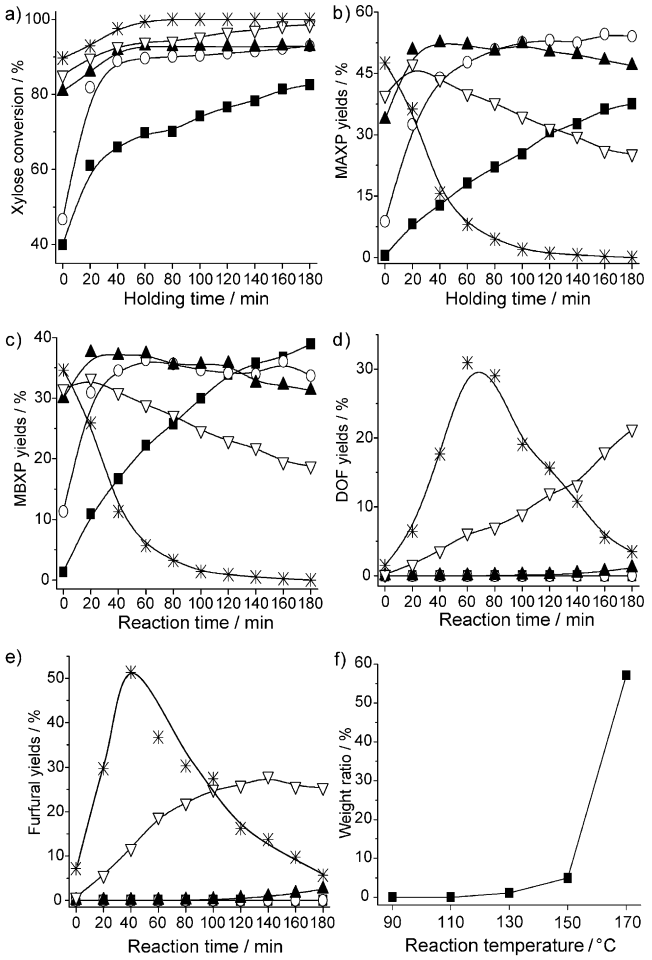
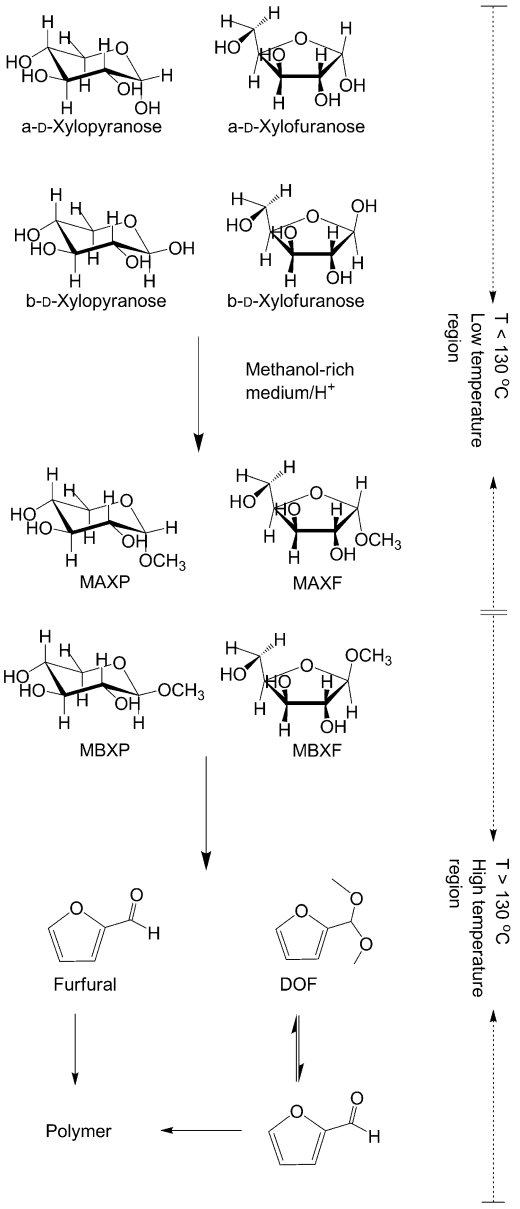


Figure 1. Effect of reaction temperature [90 (■), 110 (○), 130 (▲), 150 (▽), and 170 °C (*)] on a) xylose conversion, yields of b) MAXP, c) MBXP, d) DOF, and e) furfural as well as the weight ratio of humins to converted xylose (f). Methanol/water mass ratio: 4.5; catalyst dosage: 5 wt%; xylose loading: 5.58 wt%; reaction time: 180 min; stirring rate: 600 rpm.



Scheme 1. The main reaction pathways of xylose in methanol-rich medium.

production of different methyl xylosides is probably because of the different steric configurations of xylose in the reaction medium as shown in Scheme 1.

At 130 °C with prolonged residence time, the methyl xylosides degraded slightly, producing small amounts of 2-(dimethoxymethyl)furan (DOF, Figure 1 d) and furfural (Figure 1 e). Further increasing the temperature to 150 °C resulted in the remarkable degradation of the methyl xylosides and correspondingly produced more DOF and furfural. DOF and furfural were formed almost simultaneously, but the furfural concentration was higher than that of DOF and soon reached a maximum, whereas the DOF concentration increased monotonously. It seems that furfural was the primary product from the degradation of methyl xylosides and DOF was the secondary product from the acetalization of furfural with methanol. However, it is difficult to draw a conclusion because of the equilibrium between furfural and DOF. At 170 °C, significant amounts of furfural and DOF were formed initially, but they were soon converted to something that cannot be detected by GC–MS, which is probably the polymeric material, humins.

Figure 1 f also shows that humins formation was negligible below 130, slight at 150, and significant at 170 °C. Humins formation was closely related to the product distribution. The methanolysis of xylose to methyl xylosides below 130 °C does not lead to remarkable humins formation, whereas the productions of furfural and DOF above 150 °C was accompanied by a significant amount of humins formation. Furfural has a high tendency to polymerize in water.[21] Apparently, at 170 °C, the methanol-rich medium used did not prevent the polymerization of furfural. Although some furfural was converted to its acetal (DOF), the formation of humins consumed furfural, which would shift the equilibrium between furfural and DOF towards furfural and eventually consume DOF. These results also indicated that, in the esterification of bio-oil under similar conditions, the xylose in bio-oil could be converted into useful chemical feedstocks such as methyl xylosides, furfural, and

DOF below 150 °C, whereas it was mainly converted to humins above this temperature.

As humins formation was found to be closely related to the product distribution, which was further affected by the residence time, the change of humins formation with residence time was investigated at 170 °C. The analysis of humins formed on heating to 170 °C over one, two, and three hours at 170 °C is collected and presented in Figure 2. During heating up, the

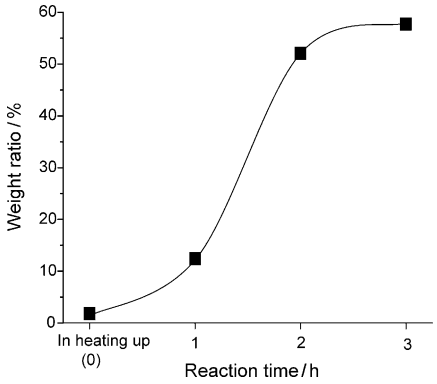


Figure 2. Effect of the residence time on humins formation (as weight ratio of humins to converted xylose) in the acid-treatment of xylose at 170 °C. Methanol/water mass ratio: 4.5; catalyst dosage: 5 wt%; xylose loading: 5.58 wt%; stirring rate: 600 rpm.

humins formation was slight and the main reaction was the methanolysis of xylose to methyl xylosides (Figures 1b and 1c), which further indicates that the methanolysis of xylose to methyl xylosides did not result in remarkable humins formation. In the first hour at 170 °C, the degradation of methyl xylosides produced a large amount of furfural and DOF (Figures 1d and 1e) and humins formation was slight. In the second hour, the furfural and DOF concentrations decreased significantly and humins formation was substantial. In the third hour, the concentrations of furfural and DOF were low and humins formation reached a plateau. These results indicated that the degradation of methyl xylosides to furfural or DOF did not lead to a significant amount of humins formation, but the further degradation of furfural and DOF mainly went to humins.

Effects of methanol/water mass ratios on xylose conversion

The acid treatment of xylose at 170 °C mainly converted xylose into humins, as presented above. Thus, the effects of the methanol/water mass ratio on the xylose conversion were investigated at 150 °C (Figure 3). High methanol/water ratios (methanol-rich medium) favored the methanolysis of xylose, resulting in faster conversion of xylose (Figure 3a) and higher concentrations of methyl xylosides (Figures 3b and 3c) and DOF (Figure 3d). In comparison, low methanol/water ratios (water-rich medium) resulted in a much slower conversion of xylose and more furfural produced (Figure 3e). The furfural production decreased with prolonged reaction time in both, methanol- and water-rich media, as it was probably converted to DOF or humins.

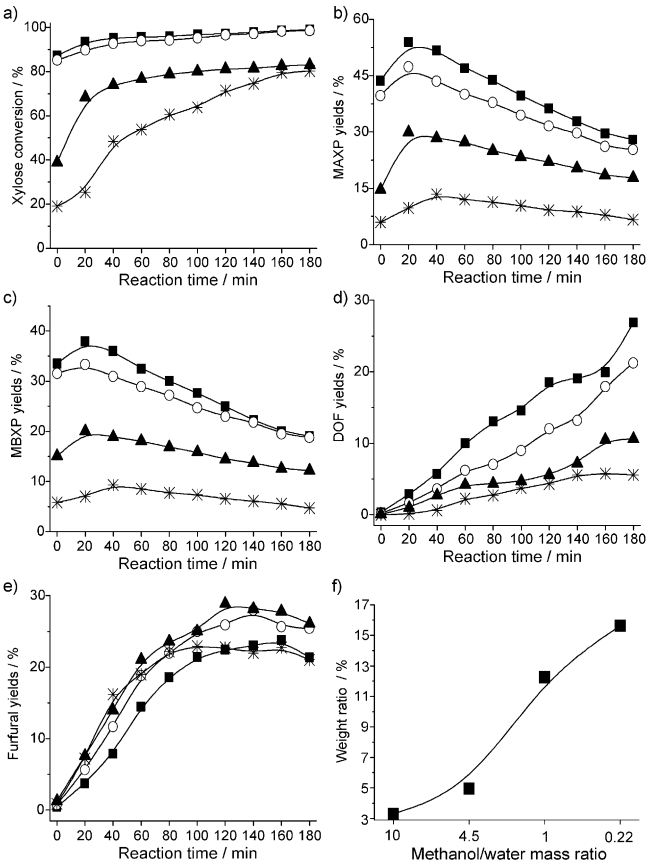
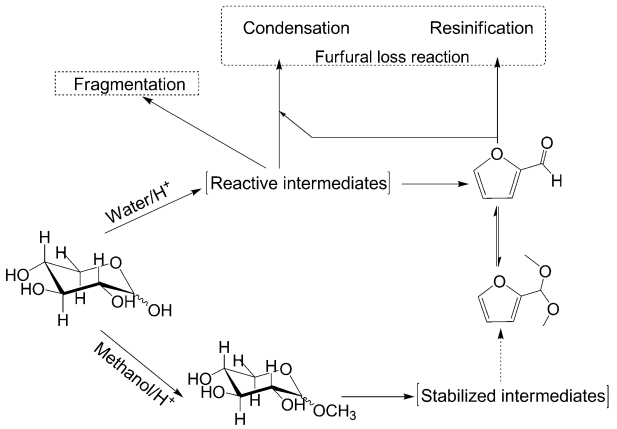


Figure 3. Effect of methanol/water mass ratios [$CH_3OH/H_2O = 10$ (■), 4.5 (○), 1 (▲), and 0.22 (*)] on a) xylose conversion, yields of b) MAXP, c) MBXP, d) DOF, and e) furfural as well as the weight ratio of humins to converted xylose (f). $T = 150$ °C; catalyst dosage: 5 wt%; xylose loading: 5.58 wt%; reaction time: 180 min; stirring rate: 600 rpm.

Figure 3f shows that humins formation was favored in the water-rich medium and suppressed in the methanol-rich medium. In the water-rich medium, high concentrations of unconverted xylose and furfural were present. Both xylose and furfural have a high tendency to polymerize to form homopolymers or a copolymer,[23,24] as shown in Scheme 2. In the methanol-rich medium, the C1 hydroxyl group of xylose and the carbonyl group of furfural are protected with methanol by etherification and acetalization reactions, which are responsible for the suppression of humins formation in the methanol-rich medium. In the water medium, the C1 hydroxyl group of xylose is easily protonated, forming a carbocation,[25] as shown in Scheme 3. The carbocation is very reactive in the acidic environment and can react with xylose to form various disaccharides or even sugar oligomers.[25] These reactions are termed "reversion reactions" and are recognized as important side reactions, which lower the utilization efficiency of sugars.[25]

To measure the formation of sugar oligomers from xylose, the acid treatment of xylose at 110 °C in water was performed. As the possible polymerized sugar products cannot be detected by GC–MS, the products were processed by the derivatization method before analysis by GC–MS. D-Xylononitrile, 4-*O*-(2,3,4-tri-*O*-acetyl-β-xylopyranosyl)-2,3,5-triacetate (XAXT, Fig-



Scheme 2. The polymerization of xylose in water and in methanol.

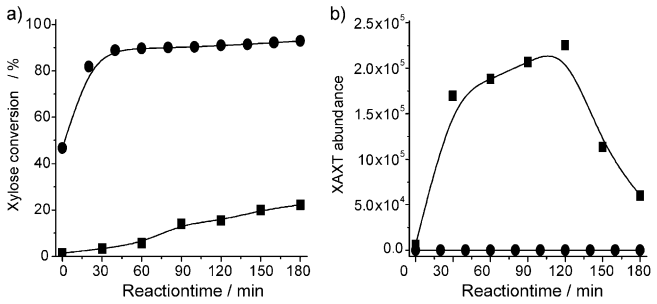


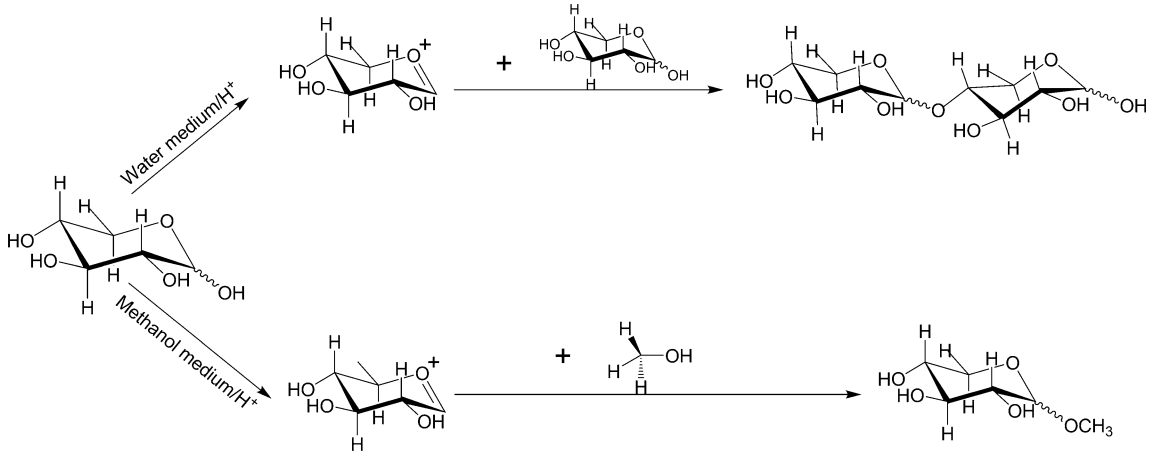
Figure 4. Acid-treatment of xylose in water (■) and in methanol-rich medium (●): Effect of reaction time on a) xylose conversion and b) XAXT abundance. In water: $T = 110\,^{\circ}C$; catalyst dosage: 5 wt%; xylose loading: 5.58 wt%; stirring rate: 600 rpm. In methanol-rich medium: $T = 110\,^{\circ}C$; catalyst dosage: 5 wt%; xylose loading: 5.58 wt%; methanol/water mass ratio: 4.5; stirring rate: 600 rpm.

ure 4b), which is the derivatization product of D-xylobiose, was detected. The structure and mass spectrum of XAXT are shown in Scheme S1 and Figure S1 in the Supporting Information. The conversion of xylose (Figure 4a) was much lower in water than that in the methanol-rich medium as methanol was very reactive to form methyl xylosides with xylose. The production of D-xylobiose reached a maximum with prolonged reaction time. D-Xylobiose contains a C1 hydroxyl group, and it was possible that D-xylobiose continued to react with xylose or other reactive intermediates to form some larger sugar oligomers. No disaccharides were detected at 110 °C in the methanol-rich medium. Apparently, the methanolysis of xylose dominated, and the formation of the disaccharides was suppressed in the presence of excess methanol.

To confirm whether the sugar oligomers acted as intermediates in the polymerization or not, the acid-treatment of xylose at 170 °C in water was performed. High xylose loadings (15 and 23 wt%) and correspondingly high catalyst loadings were used as the high concentration of xylose favored the formation of sugar oligomers. The results presented in Figure S2 showed that D-xylobiose was also formed, reached a maximum, and then decreased significantly. A similar case was that of furfural (Figure S2); at 170 °C in the acidic medium, the dehydration of xylose to furfural and the subsequent polymerization of furfural and/or the sugar oligomers dominated, which led to the formation of humins as the main product. The weight ratio of the humins to the xylose converted in the experiment with a xylose loading of 23 wt% (65%) was higher than that with a xylose loading of 15 wt% (61%). The high initial xylose loading produced more polymeric intermediates and favored polymerization reactions.

In the methanol-rich medium, methanol will react with xylose to form methyl xylosides because of the high reactivity and the small steric effect of methanol. The methyl xylosides were relatively stable and would not easily be converted back in the methanol-rich medium to the reactive xylose carbocation (Scheme 3). Consequently, the formation of disaccharides or sugar oligomers in the methanol-rich medium was suppressed. Furthermore, the copolymer formed from the condensation of xylose and furfural may also be suppressed because of the stabilization of xylose as methyl xylosides.

In the methanol-rich medium with prolonged residence time, instead of conversion back to xylose, the methyl xylosides continued to degrade to some intermediates and eventually to DOF and furfural (Scheme 2). It is believed that the methanol also helped to stabilize the intermediates from the



Scheme 3. The formation of disaccharides in water and methyl xylosides in methanol.

degradation of methyl xylosides, which might also contribute to the suppression of humins formation. Furfural is another precursor of humins. In the methanol-rich medium, some of the carbonyl groups in furfural were protected with methanol by acetalization, which may affect the tendency of furfural to polymerize. To further investigate the effects of this protection, the reactions of furfural with pure methanol and water were performed, respectively.

Reaction pathways of furfural in aqueous and methanolic media

The reactions of furfural with water and methanol were performed at 170 °C as the humins formation from furfural is expected to be significant at this temperature. Furfural conversion and the product distribution are presented in Figure 5. Most furfural was converted at the end (reaction time: 180 min) in both water and methanol (Figure 5a). One difference is that DOF was produced as the main intermediate in methanol (Figure 5b). Although some other products were formed, their concentrations were small or at trace levels. The main product was humins, the weight of which with respect to the loaded furfural was 55.67% in water and 50.55% in methanol. The slight difference in humins formation indicates that the conversion of furfural to DOF (and protection of the carbonyl group) did not effectively suppress polymerization at 170 °C. There is a reaction equilibrium between furfural and DOF in methanol, and the polymerization of furfural and the acetalization of furfural to DOF occurred in parallel. Although most furfural was initially converted to DOF in methanol, the polymerization of furfural consumed furfural, which would shift the reaction equilibrium from DOF to furfural with prolonged residence time and eventually consume most of the DOF (Scheme 4). Thus, the long residence time in acidic medium and the high reaction temperature still led to humins formation from furfural. With a short residence time, the conversion of furfural into DOF probably helps to suppress humins formation from furfural as the formation of DOF decreases the concentration of furfural in the reaction medium.

In addition to humins formation, some interesting minor products were also detected. In water, formic acid was detected (Figure 5c), which is known as a product in the degradation or polymerization of furfural.[26] However, the formation of levulinic acid (Figure 5d), a platform molecule from the hydrolysis of C6 carbohydrates,[27] from furfural was unexpected. The hydrogenation of furfural to 2-furylmethanol followed by hydrolysis or methanolysis produces levulinic acid or its ester.[28–30] However, 2-furylmethanol was not detected, which was probably because formic acid, the potential hydrogen donor,[31–33] reduced furfural to some intermediates and then to levulinic acid in the acidic environment. In methanol, instead of levulinic acid, methyl levulinate was produced (Figure 5e), which was the product from levulinic acid and methanol. In addition,

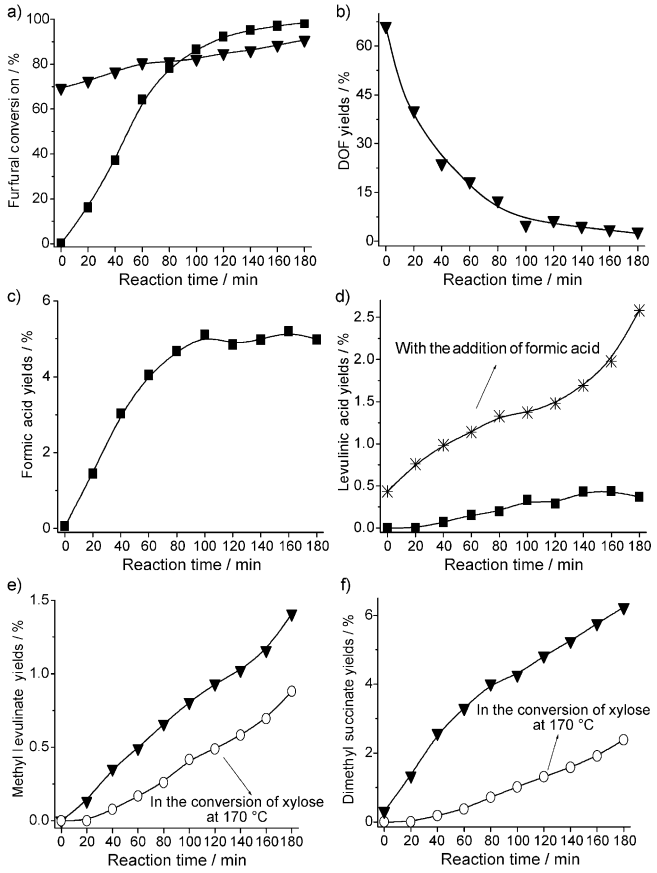
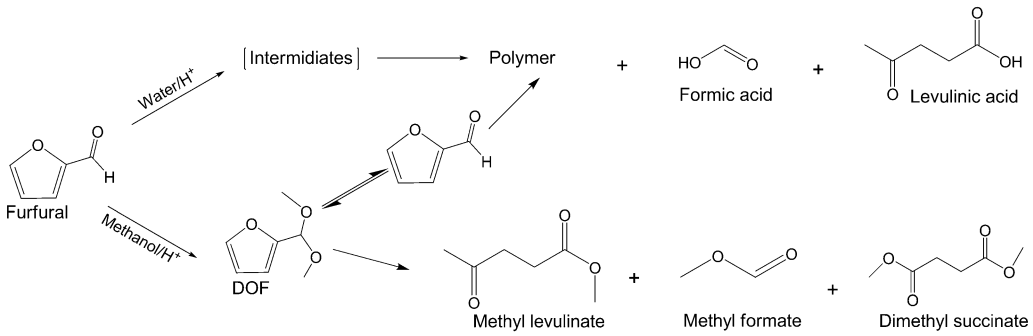


Figure 5. Acid treatment of furfural in water (■) and in methanol (▼). Effect of reaction time on a) furfural conversion and yields of b) DOF, c) formic acid, d) levulinic acid, e) methyl levulinic acid, and f) dimethyl succinate. Furfural initial concentration: 5.58 wt%; $T = 170$ °C; catalyst dosage: 5 wt%; stirring rate: 600 rpm.



Scheme 4. The reaction pathways of furfural in water and in methanol.

methyl levulinate was also detected in the conversion of xylose at 170 °C in the methanol-rich medium. In addition to methyl levulinate, methyl formate was also detected in trace amounts (not shown).

To measure the effect of formic acid on the formation of levulinic acid from furfural, 4.5 wt% of formic acid was added to the water medium to catalyze the conversion of furfural (the other conditions were the same). The yield of levulinic acid is presented in Figure 5d. The formic acid added was not markedly consumed, but its presence facilitated the production of levulinic acid in low concentration. The polymerization of furfural and the formation of levulinic acid occurred in parallel. The domination of the polymerization of furfural suppressed the conversion of furfural to levulinic acid. Therefore, a highly active hydrogenation catalyst may be required to facilitate the decomposition of formic acid to hydrogen to promote the production of levulinic acid from furfural. In addition to these products, dimethyl succinate was also present in the conversion of furfural in methanol and in the conversion of xylose in methanol-rich medium at 170 °C (Figure 5f). Dimethyl succinate should be the product of the reaction between methanol and succinic acid, but succinic acid was not detected in the conversion of furfural in water. Similarly, the high tendency of furfural to polymerize suppressed the formation of dimethyl succinate.

Effects of catalyst dosage on product distribution and humins formation

The amount of catalyst may influence the reaction rates of hydrolysis, methanolysis, and polymerization. Hence, the catalyst dosage was expected to significantly affect the product distributions and the humins formation. The effect of catalyst dosage on xylose conversion in the methanol-rich medium was investigated at 150 °C with catalyst dosages ranging from 2 to 8 wt% (Figure 6). Higher catalyst dosages promoted the conversion of xylose, but the effects were relatively small (Figure 6a). However, the degradation of methyl xylosides was greatly affected (Figures 5b and 6c). The degradation of methyl xylosides involved the protonation of three hydroxyl groups and their subsequent dehydration. Hence, methyl xyloside degradation was sensitive to catalyst dosage and favored by high catalyst dosages. Consequently, more DOF and furfural were produced with the high catalyst dosage of 8 wt% (Figures 6d and 6e). The humins formation presented in Figure 6f showed that the higher the catalyst dosage used, the more humins were formed. With a low catalyst dosage (2 wt%), the degradation of methyl xylosides was much slower. Consequently, the concentrations of methyl xylosides were high and those of furfural and DOF were low, which were the main reasons for the reduced humins formation with this low catalyst loading. Of course, prolonged residence time might also increase humins formation with a catalyst dosage of 2 wt%. However, the above results support that the conversion of xylose to methyl xylosides lowered the reactivity of xylose to polymerization and consequently suppressed humins formation.

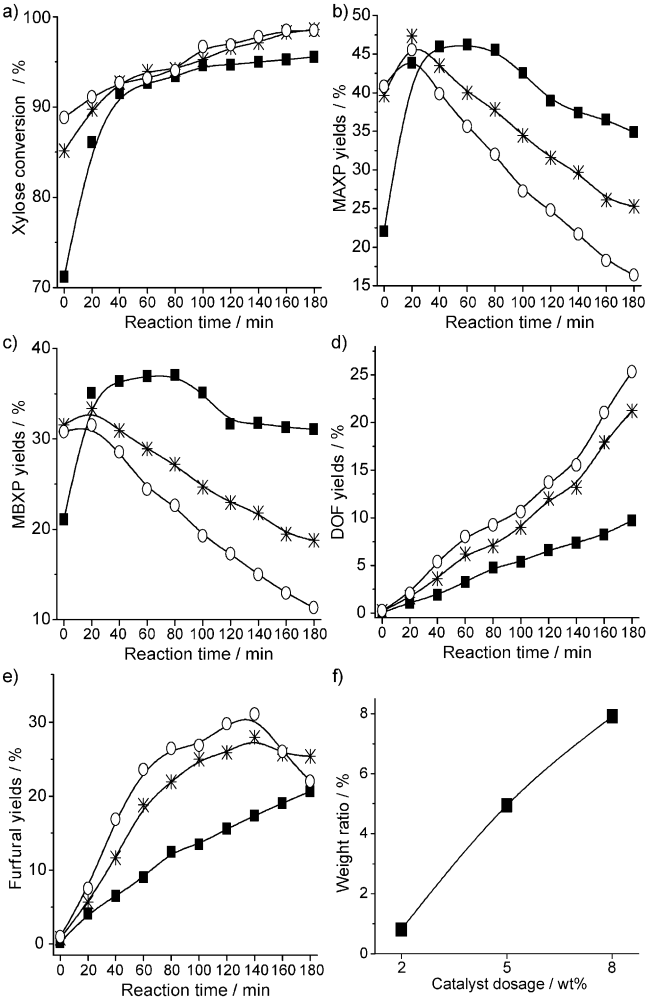


Figure 6. Effect of catalyst dosage [2 (■), 5 (*), and 8 wt% (●)] on a) xylose conversion, yields of b) MAXP, c) MBXP, d) DOF, and e) furfural as well as the weight ratio of humins to converted xylose (f). $T = 150$ °C; methanol/water ratio: 4.5; xylose loading: 5.58 wt%; stirring rate: 600 rpm.

Characterizations of humins with FTIR and UV fluorescence spectroscopy

The functional groups of the humins were characterized by using FTIR and UV fluorescence spectroscopy. The FTIR spectroscopic results (Figure S3 and Table 1) showed that the humins contain a wide range of functional groups including hydroxyl groups, carbonyl groups, carbon–carbon double bonds, aliphatic C–H bonds, and aromatic rings. UV fluorescence spectroscopy showed a strong excitation from $\lambda = 330$–500 nm (Figure S4), which indicated that the humins contain large conjugated π-bonded systems.[34] Thus, humins is a polymeric material with various functional groups.

Conclusions

Humins formation in the acid treatment of xylose was investigated by variation of the reaction parameters. A high reaction temperature, long residence time, low methanol/water mass

Table 1. Assignments of the FTIR peaks of the humins.

$\tilde{\nu}$ [cm^{-1}]	Assignment
3660–3590	O–H stretch: alcohols, phenols
3040–3000	C=C–H stretch: aromatics, unsaturated bonds
2990–2800	C–H stretch: aliphatics
2700–2500	OH stretch
1820–1650	C=O stretch: carbonyls
1650–1500	C=C stretch: substituted aromatics
1420–1410	CH_2 deformation: unsaturated bonds
1250–1000	C–O stretch, O–H deformation: alcohols, ethers
900–690	C–H out of plane deformation: substituted aromatics

ratio, and high catalyst dosage were favorable for humins formation. Both xylose and furfural contributed to polymerization in water. In the methanol-rich medium, xylose was converted to methyl xylosides, which stabilized xylose and suppressed the formation of sugar oligomers and polymerization reactions. Although furfural can be converted into 2-(dimethoxymethyl)-furan (DOF) in the methanol-rich medium, this did not remarkably suppress polymerization at 170 °C because of the shift of the reaction equilibrium from furfural to DOF with prolonged residence time. These results are helpful to understand the reaction pathways of xylose in the esterification of bio-oil and to select the appropriate reaction conditions to produce platform molecules and avoid the occurrence of side reactions. The acid treatment of furfural also produced methyl levulinate in methanol and levulinic acid in water, which was found to be catalyzed by the degradation product of furfural, formic acid. More attention may need to be paid to this reaction pathway as methyl levulinate and levulinic acid are platform molecules for diverse chemicals.

Experimental Section

Materials

All chemicals used in this study were of analytical grade and used without further purification. 2-(Dimethoxymethyl)furan (DOF) was purchased from LC Scientific Inc. (Canada). Methyl-α-D-xylopyranoside (MAXP) and methyl-β-D-xylopyranoside (MBXP) were purchased from Carbosynth Limited (UK). Xylose, furfural, methyl levulinate, levulinic acid, formic acid, and dimethyl succinate were purchased from Sigma Aldrich. Methanol was obtained from Merck Australia. Amberlyst 70 (Rohm & Haas), a commercial solid acid catalyst with a maximum operating temperature of 190 °C and concentration of acidic sites of $\geq$2.55 eq kg^{-1}, was used without further pretreatment. The stability of Amberlyst 70 and the leaching of the $-SO_3H$ group were tested, and the results showed that the decomposition of the catalyst and the leaching of the $-SO_3H$ group were insignificant under the reaction conditions used in this study.

Experimental procedures

The experiments were performed in a stainless steel, high-pressure batch reactor (Parr 4572, Parr Instrument Co.). In each experiment, given amounts of xylose, methanol, water, and Amberlyst 70 were mixed and introduced into the reactor. The volume of the reactants was typically approximately 390 mL. The initial concentration of xylose was 5.58 wt% (ca. 18.98 g) for most of the experiments, which is specified in the figure legends. The autoclave was purged with nitrogen three times after the introduction of reactants and then heated to the desired temperature at 6 °C min^{-1} with a stirring rate of 600 rpm. The selection of the stirring rate of 600 rpm was based on the observation that no mass transfer limitations were found with stirring rates above 300 rpm in preliminary experiments. A sample was taken immediately after reaching the reaction temperature, and further samples were taken at 20 min intervals. The holding time at the reaction temperature was 180 min for all experiments. The initial pressure in autoclave was approximately 1 bar before heating, and the final pressure depended on the reaction temperature and the reaction medium. The humins formed as isolated particles, deposited on the catalyst, or adhered to the reactor wall were collected after the reactor cooled and dried in a vacuum oven at 100 °C for 4 h to constant weight to determine the amount of the humins formed.

Analytical methods

Samples were analyzed by using a Hewlett–Packard GC–MS (HP6890 series GC with an HP5973 MS detector) with a capillary column (HP-INNOWax, length = 30 m, internal diameter = 0.25 mm, film thickness = 0.25 μm). Standard solutions covering the concentration range of the samples were used to obtain calibration curves to calculate the concentrations of the compounds of interest. The sample (1 μL) was injected into the injection port set at 250 °C with a split ratio of 50:1. The column was operated in a constant flow mode using 3.0 mL min^{-1} of helium as the carrier gas. The column temperature was initially maintained at 40 °C for 3 min before increasing to 260 °C at a heating rate of 15 °C min^{-1}. The identification of each compound was achieved by matching its mass spectrum with that in the spectral library and was confirmed by injecting the standard where available. A derivatization method was used to determine xylose, broadly following the procedure in the literature.[35] A typical chromatograph after derivatization of the products is shown in Figure S5. FTIR spectra of the humins were recorded by using a Perkin–Elmer Spectrum GX FTIR/Raman Spectrometer with a spectral resolution of 4 cm^{-1} at room temperature. The spectrum represents the average of at least six scans. The weight ratio of the humin-type polymer to KBr was 0.5 wt%. The UV fluorescence spectra of the humins were recorded by using a Perkin–Elmer LS50B spectrometer. The synchronous spectra were recorded with a constant energy difference of -2800 cm^{-1}. The slit widths were 2.5 nm and the scan speed was 200 nm min^{-1}.

The definitions of xylose conversion and product yields were as follows:

$$\text{Conv. (mol\%)} = \frac{\text{1}-\text{mol of xylose in product}}{\text{mol of xylose loaded in reactor}} \times 100\,\% \quad (1)$$

$$\text{Yield (mol\%)} = \frac{\text{mol of product produced}}{\text{mol of xylose loaded in reactor}} \times 100\,\% \quad (2)$$

Acknowledgements

We gratefully acknowledge the financial support of the Australian Government through the Second Generation Biofuels Research and Development Grant Program and the International Science Linkages (ISL) Program.

Keywords: alcohols · carbohydrates · heterogeneous catalysis · polymerization · solvent effects

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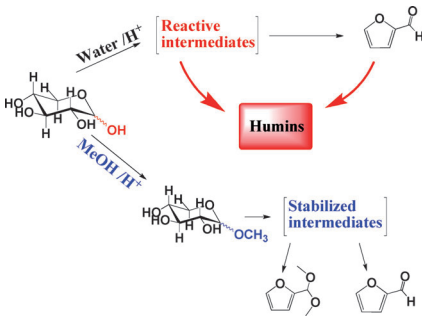
Received: November 19, 2011
Published online on ■■ ■■, 0000

Methanolysis makes the difference: In a methanol/water medium, the conversion of xylose to methyl xylosides protects the C1 hydroxyl group of xylose, which stabilizes xylose and suppresses the formation of sugar oligomers and polymerization reactions.



*X. Hu, C. Lievens, C.-Z. Li**

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Acid-Catalyzed Conversion of Xylose in Methanol-Rich Medium as Part of Biorefinery

