Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Informations

Dehydration of Biomass to Furfural Catalyzed by Reusable Polymer Bound Sulfonic Acid (PEG-OSO_3H) in Ionic Liquid

1. General information.

All reactions were performed using standard Schlenk glass tube. All materials were obtained from commercial suppliers and were used without further purification, Corn stover, corncob, pinewood, poplar, switchgrass and straw were obtained locally (Lanzhou, China).

Unless otherwise noted, furfural was extracted with diethyl ether absolute, concentrated with a rotary evaporator, and dried under vacuum at 50 °C. NMR spectra were recorded at 400 (^1H) and 101 (^{13}C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ as solvent and TMS as internal standard. Mass-spectra were recorded on a Bruker APEX Ⅱ instrument. The products was analyzed by HPLC with Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45: 90) were used as the mobile phase at a flow rate of 0.6 mL min^{-1}. The following abbreviations were used to describe peak patterns where appropriate: singlet (s), doublet (d), triplet (t), multiplet (m).

Furfural was quantified with calibration curves generated from commercially available standards.

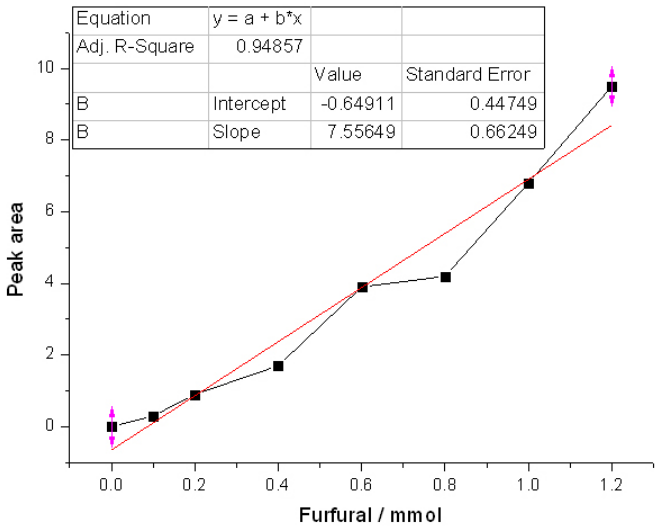


Fig. S1. Calibration curves of furfural.

The concentrations of products were calculated from HPLC-peak integrations and used to calculate molar yield.

The yield of furfural were defined as follows:

Conversion = moles of pentoses reacted / moles of starting pentoses

Furfural yield = moles of furfural produced / moles of starting pentoses

For biomass, furfural yields were defined as follows:

$$\text{Furfural yield} = \frac{\text{moles of furfural produced} \times 0.096\ \text{g/mmol}}{0.3\text{g}} \times 100\,\%$$

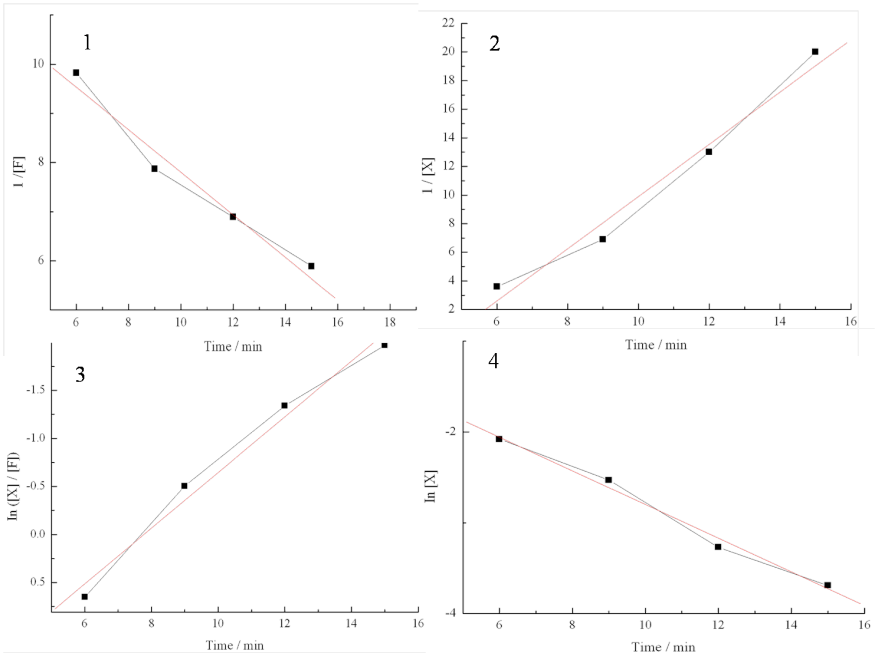


Fig. S2. Plots of xylose and furfural for calculations of k_1, k_2 and k_3.

2. Structural and textural characterization

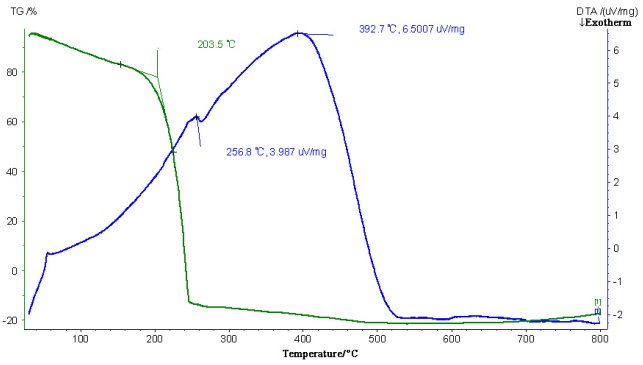
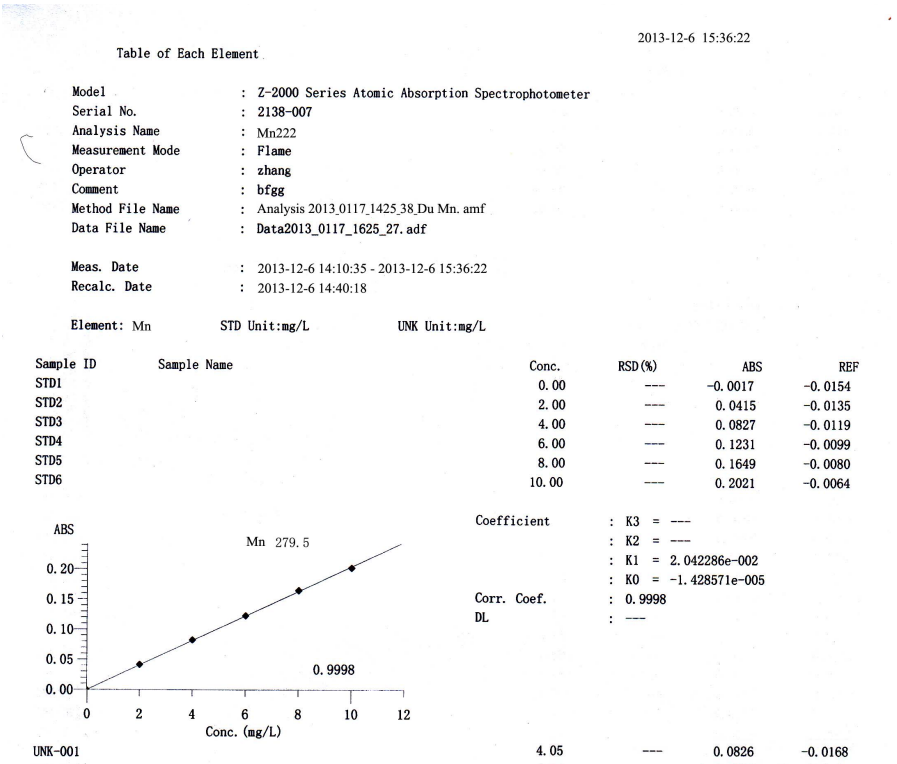


Fig. S3. TG curves of PEG-OSO_3H sample.

The structure of PEG-OSO_3H has been confirmed in our previous jobs.[1,2]



2013-12-6 15:36:22

Table of Each Element

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Serial No. : 2138-007
Analysis Name : Mn222
Measurement Mode : Flame
Operator : zhang
Comment : bfgg
Method File Name : Analysis 2013_0117_1425_38_Du Mn. amf
Data File Name : Data2013_0117_1625_27. adf

Meas. Date : 2013-12-6 14:10:35 - 2013-12-6 15:36:22
Recalc. Date : 2013-12-6 14:40:18

Element: Mn STD Unit:mg/L UNK Unit:mg/L

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0. 00	---	-0. 0017	-0. 0154
STD2		2. 00	---	0. 0415	-0. 0135
STD3		4. 00	---	0. 0827	-0. 0119
STD4		6. 00	---	0. 1231	-0. 0099
STD5		8. 00	---	0. 1649	-0. 0080
STD6		10. 00	---	0. 2021	-0. 0064

Coefficient : K3 = ---
: K2 = ---
: K1 = 2. 042286e-002
: K0 = -1. 428571e-005
Corr. Coef. : 0. 9998
DL : ---

UNK-001	4. 05	---	0. 0826	-0. 0168

Fig. S4. The AA analysis of $MnCl_2$ recovery.

3. Typical Procedure for the Catalysis

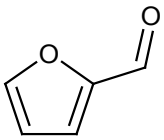
Pentoses (0.5 mmol), PEG-OSO_3H (0.3 g, 0.1 mmol), $MnCl_2$ (0.15 mmol), [BMIM]PF_6 (2 mL) were added to 15 mL standard Schlenk glass tube; the reaction was heated to 120 °C for 18 min. In a typical experiment for the transformation of biomass in [BMIM]PF_6 system, a 15 mL standard Schlenk glass tube was charged with biomass (0.3 g), PEG-OSO_3H (0.1 mmol), $MnCl_2$ (0.15 mmol), [BMIM]PF_6 (2 mL); the reaction was heated to 120 °C for 18 min.

Dehydration of xylose to furfural using PEG-OSO_3H as catalyst. A mixture of xylose (0.5 mmol), $MnCl_2$ (0.15 mmol) and PEG-OSO_3H (0.1 mmol) in [BMIM]PF_6 was stirred at 120 °C for 18 min. After completion monitored by TLC, the resulting mixture was cooled to room temperature immediately. The mixture was extracted 3 times with 2 mL of diethyl ether absolute. The combined organic phase was dried over Na_2SO_4. After evaporating the solvent a yellowish oily matter, furfural (73% isolated yield, 100% purity by HPLC) obtained and dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): 6.62 (t, 1H, *J*=4.0 Hz, Furan-H-4), 7.28 (d, *J*=6.0 Hz, 1H, Furan-H-3), 7.71 (d, *J*=4.0 Hz, 1H, Furan-H-5), 9.67 (s, 1H, CHO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): 112.50, 121.00 (Ar), 148.02 (Ar),

152.87 (Ar), 177.81 (CHO) ppm. FTIR (KBr) (ν, cm-1): 1020 (C-O-C), 1520 (C=C), 1671 (-CHO), 2848, 2806 ($-CH_2$), 3388 (-OH).

All the products were confirmed by ^{1}H NMR, ^{13}C NMR, HRMS (ESI), elemental analysis and HPLC analysis.

Furfural



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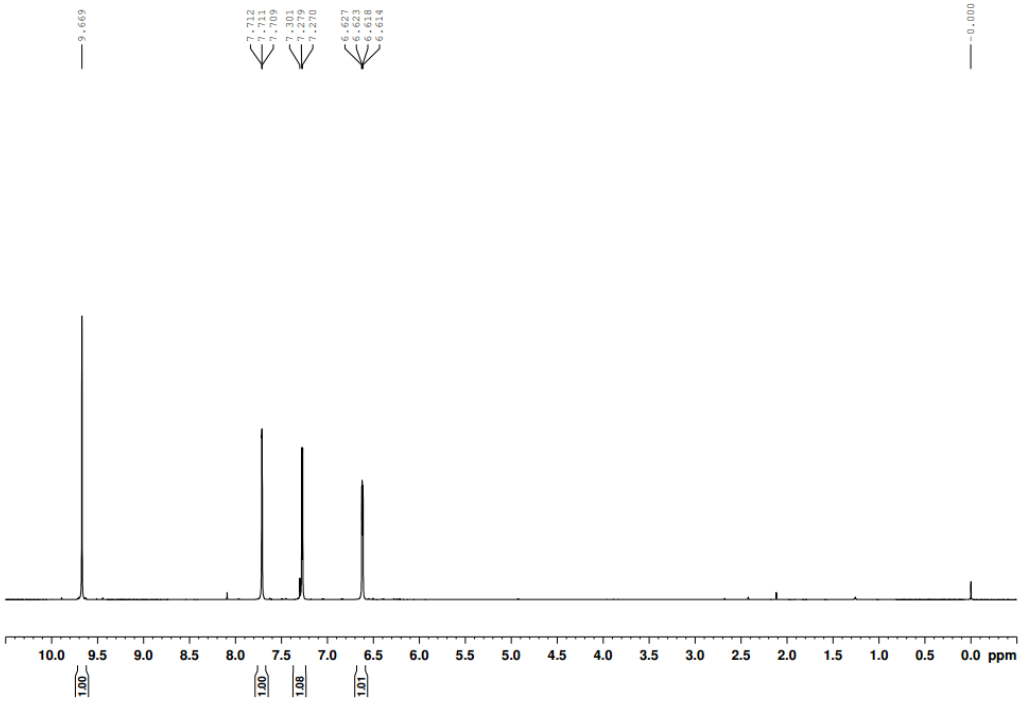

Fig. S5. ^{1}H NMR.

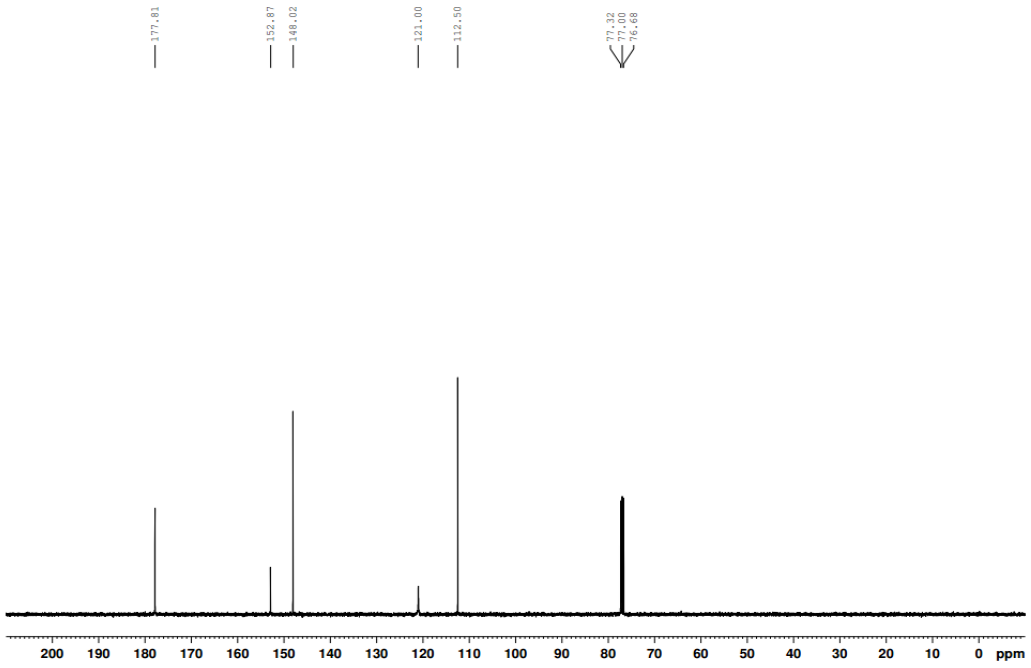

Fig. S6. ^{13}C NMR.

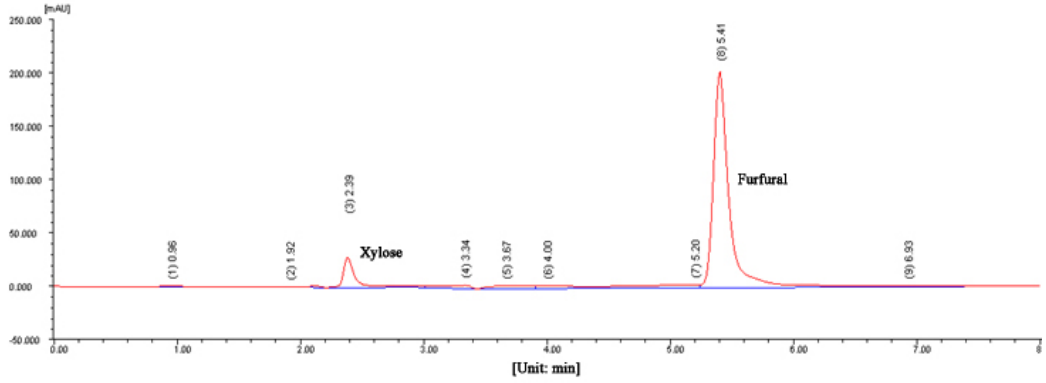

Fig. S7. Detecting of residual xylose using HPLC. Analyses were performed with a Kromasil-C_{18}-5µ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45: 90) were used as the mobile phase at a flow rate of 0.8 mL min^{-1}.

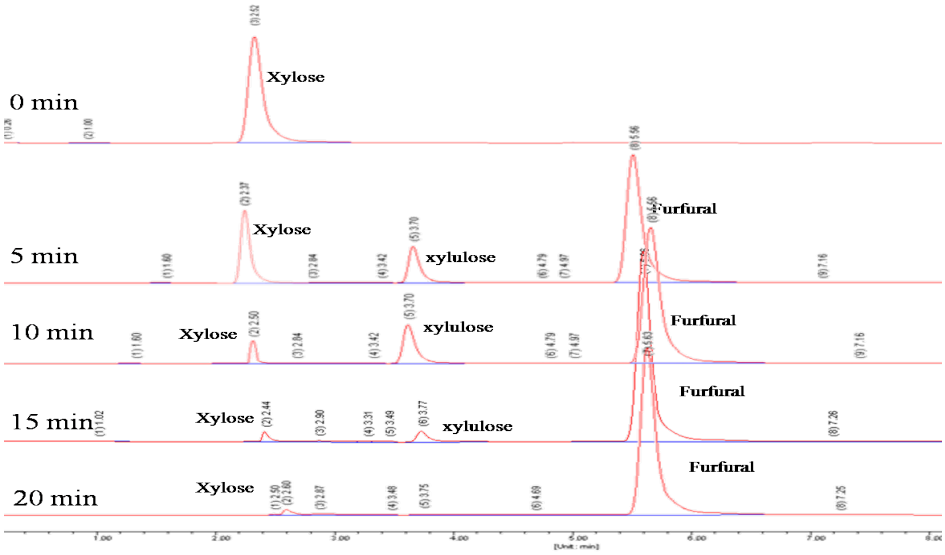

Fig. S8. Separation of pentoses using Kromasil-C_{18}-5μ column by the HPLC. Analyses were performed with a Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45: 90) were used as the mobile phase at a flow rate of 0.6 mL min^{-1}.

Dehydration of raw biomass to furfural using PEG-OSO_3H as catalyst.

Finally, we applied the polymer bound sulfonic acids catalyst (PEG-OSO_3H) to raw biomass. A 15 mL standard Schlenk glass tube was charged with raw biomass (0.3 g), PEG-OSO_3H (0.1 mmol), $MnCl_2$ (0.15 mmol), [BMIM]PF_6 (2 mL); the reaction was heated to 120 °C for 18 min. After completion monitored by TLC, the resulting mixture was filtered and washed with diethyl ether absolute. Then the filtrate was extracted with 3×2 mL of diethyl ether absolute and the organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Then the amount of furfural was analyzed by HPLC with Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45: 90) were used as the mobile phase at a flow rate of 0.6 mL min^{-1}.

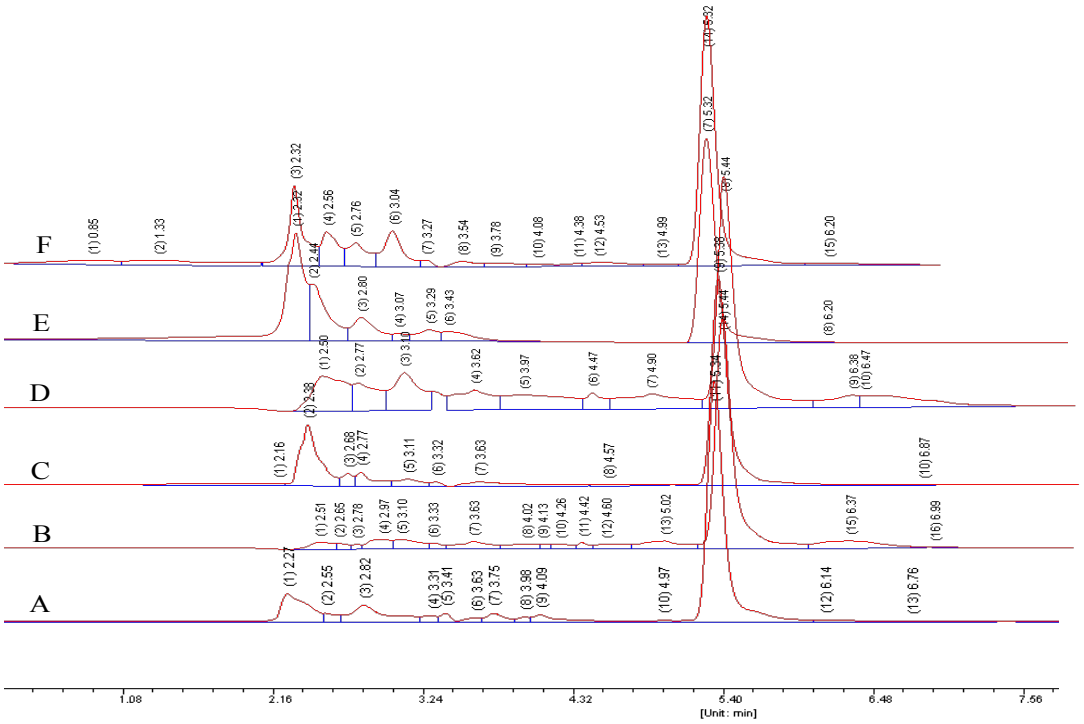

Fig. S9. Refractive index HPLC trace of raw biomass reaction mixture. Analyses were performed with a Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45: 90) were used as the mobile phase at a flow rate of 0.6 mL min^{-1}. (A) Synthesis of furfural from corn stover with PEG-OSO_3H in [BMIM]PF_6. (B) Synthesis of furfural from corncob with PEG-OSO_3H in [BMIM]PF_6. (C) Synthesis of furfural from pinewood with PEG-OSO_3H in [BMIM]PF_6. (D) Synthesis of furfural from poplar with PEG-OSO_3H in [BMIM]PF_6. (E) Synthesis of furfural from switchgrass with PEG-OSO_3H in [BMIM]PF_6. (F) Synthesis of furfural from straw with PEG-OSO_3H in [BMIM]PF_6.

References

1 X. C. Wang, Z. J. Quan, F. Wang, M. G. Wang, Z. Zhang, Z. Li, *Synth. Commun*. **2006**, *36*, 451–456.

2 Z. J. Quan, Y. X. Da, Z. Zhang, X. C. Wang, *Catal. Commun*. **2009,** *10*, 1146–1148.